ABANT IZZET BAYSAL UNIVERSITY
THE GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

# SYNTHESIS OF BIS-(*P*-ARYL) AMIDES: NEW PHASE-SELECTIVE LOW MOLECULAR WEIGHT ORGANOGELATORS

MASTER OF SCIENCE

BURCU BİLALOĞLU

BOLU, DECEMBER 2017

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## APPROVAL OF THE THESIS

**SYNTHESIS OF BIS-(*p*-ARYL) AMIDES: NEW PHASE-SELECTIVE LOW MOLECULAR WEIGHT ORGANOGELATORS** submitted by **Burcu BİLALOĞLU** in partial fulfillment of the requirements for the degree of **Master of Science** in **Department of Chemistry, The Graduate School of Natural and Applied Sciences of ABANT IZZET BAYSAL UNIVERSITY in 28/12/2017** by

| **Examining Committee Members** | **Signature** |
|---|---|
| Supervisor<br>Assoc. Prof. Öznur DEMİR-ORDU<br>**Abant İzzet Baysal University** | ..... |
| Member<br>Assoc. Prof. Muhammet YILDIRIM<br>**Abant İzzet Baysal University** | ..... |
| Member<br>Assist. Prof. Abdulkadir ALLI<br>**Düzce University** | ..... |

**Graduation date:** ...../...../20....

**Doç. Dr. Ömer ÖZYURT** .....

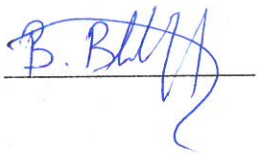
**Director of Graduate School of Natural and Applied Sciences**

To my family

**DECLARATION**

I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Burcu BİLALOĞLU



# ABSTRACT

## SYNTHESIS OF BIS-(*p*-ARYL)AMIDES: NEW PHASE-SELECTIVE LOW MOLECULAR WEIGHT ORGANOGELATORS

**MSC THESIS**
**BURCU BİLALOĞLU**
**ABANT IZZET BAYSAL UNIVERSITY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES**
**DEPARTMENT OF CHEMISTRY**
**(SUPERVISOR: ASSOC. PROF. ÖZNUR DEMİR-ORDU)**
**BOLU, DECEMBER 2017**

Low molecular weight organogelators (LMWO) are a family of organic molecules that can gel organic solvents at low concentrations. Organogelators create a three dimensional network via noncovalent interactions, such as hydrogen bonding, van der Waals interaction, $\pi$-$\pi$ stacking, or dipole-dipole interaction etc.

Organogels are composed of self-assembled LMWOs into entangled three-dimensional networks with solvent molecules entrapped inside through weak intermolecular interactions. The main characteristic properties of gels formed by LMWOs are their thermo-reversible gel-to-sol transition: the gel can be transformed into sol and then back into gel repeatedly by heating the sample above and below the sol-gel transition temperature. Although the self-assembly process can not be fully understood, some of the factors affecting the process are: solvent type, concentration, temperature and especially molecular structure and it became clear that there are two important characteristics of a good gelling agent; strong self-complementarity and unidirectional interactions. Amide functionality fulfills these requirements. Because amide-amide type compounds have four potential hydrogen bonding sites, bis-amides can form very strong gels.

In recent years there has been significant progress in design of new gelling agents. Gels formed by low molecular weight organic compounds have important applications for new organic soft materials. Examples of these areas include drug delivery, cosmetics, sensor systems, phase-selective cleaners. Phase selective organogelators have been attracting a lot of attention in water purification and oil-spill recovery. These organogelators are preferred because they are cheaper and simpler to use than currently used methods.

With this aim, the main purpose of this project is to obtain bis-amide-based materials that can be used in environmental applications. These materials obtained in "sorbent" and "solidifier" forms were used in order to remove vegetable/petroleum oil spills from water. In this study, first, new bis-amide derivatives were synthesized by the reaction of *para*-substituted benzoyl chlorides with 1,3-diamino propane in the presence of triethyl amine in chloroform and their organogelation behavior as solidifiers were studied by test tube inversion method in common organic solvents, vegetable oils (olive oil, sunflower oil, nut oil etc.), and petroleum products (gasoline, diesel etc.). It was found that the length of *p*-alkyl tail had an influence on organogel formation.

Nano-fibrous and porous sorbents having high surface area could be obtained by drying the gels and used in the removal process since heating-cooling prosess is required for the formation of organogels via solidification which makes the removal of oil difficult in environmental applications. In this study, oil removal capacity of the sorbents were also determined for selected xerogels. The morphology of gels were examined by optical microscopy.

**KEYWORDS:** Low molecular weight organogelators, Bis-amides, Organogels, self-assembly, phase selective organogelation, solidifiers, xerogels as nano-fibrous and porous sorbents, optical microscopy.

# ÖZET


## BIS-(*P*-ARIL) AMIDLERIN SENTEZİ: YENI FAZ SEÇİCİ DÜŞÜK MOLEKÜLER AĞIRLIKLI ORGANOJELLEŞTİRİCİLER

**YÜKSEK LİSANS TEZİ**
**BURCU BILALOĞLU**
**ABANT İZZET BAYSAL ÜNİVERSİTESİ FEN BİLİMLERİ ENSTİTÜSÜ**
**KİMYA ANABİLİM DALI**
**(TEZ DANIŞMANI: DOÇ. DR. ÖZNUR DEMIR-ORDU)**
**BOLU, ARALIK - 2017**

Düşük molekül ağırlıklı organojelleştiriciler (DMAO), organik çözücüleri düşük konsantrasyonlarda jelleştirebilen organik molekül ailesidir. Organojelleştiriciler, hidrojen bağı, van der Waals etkileşimi, π-π istifleme veya dipol-dipol etkileşimi gibi kovalent olmayan etkileşimler yoluyla üç boyutlu bir ağ oluşturur.

Organojeller, öz-toparlanmayla bir araya getirilmiş DMAO'lardan zayıf molekül içi etkileşimler yoluyla hapsolan çözücü moleküllerinin iç içe geçmiş üç boyutlu ağ yapısı oluşturmasıyla meydana gelir. DMAO'ların oluşturduğu jellerin temel karakteristik özellikleri termo-tersinir sol-jel geçişidir: jel sol haline dönüştürülebilir ve sol- jel sıcaklığının üstünde ve altında örneğin ısıtılmasıyla tekrar jel haline getirilebilir. Öz-toparlanma süreci tam olarak anlaşılmamış olsa da, süreci etkileyen faktörlerden bazıları: çözücünün türü, konsantrasyon, sıcaklık ve özellikle molekül yapısıdır. İyi bir jelleştirici maddenin iki önemli özelliği olduğu açıktır; güçlü öz-toparlanma ve tek yönlü etkileşimler. Amid işlevselliği bu gereksinimleri karşılar özelliktedir. Amid-amid tipi bileşiklerin dört potansiyel hidrojen bağlanma bölgesine sahip olmaları nedeniyle bis-amidler çok güçlü jel oluşturabilirler.

Son yıllarda yeni jelleştirici ajanların tasarımında belirgin ilerleme kaydedilmiştir. Düşük molekül ağırlıklı organik bileşiklerden oluşan jeller yeni organik yumuşak malzemeler için önemli uygulamalar içerir. Bu alanlara örnek olarak ilaç taşınımı, kozmetik, sensör sistemleri, faz seçici temizleyiciler verilebilir. Faz seçici organojelleştiriciler, su arıtma ve petrol sızıntısının giderilmesinde çok dikkat çekmektedir. Bu organojelleştiriciler hali hazırda kullanılan yöntemlere göre daha ucuz ve daha basit oldukları için tercih edilirler.

Bu amaçla, çevresel uygulamalarda kullanılabilcek bis-amid esaslı malzemeler elde etmek bu çalışmanın temel amacıdır. "Adsorban" ve "katılaştırıcı" formlarında elde edilen bu malzemeler sudan bitkisel/petrol yağ atıklarının uzaklaştırılması için kullanılır. Bu projede öncelikle, yeni bis-amid türevleri, kloroform içinde trietil amin varlığında 1,3-diamino propan ile para-sübstitüentli benzoil klorürlerin reaksiyonu ile sentezlenmiş ve "katılaştırıcı" olarak organojelleşme davranışları, organik çözücüler, bitkisel yağlar (zeytin yağı, ayçiçeği yağı, fındık yağı vb.) ve petrol ürünleri (benzin, dizel vb.) içinde test tüp ters çevirme yöntemi ile incelenmiştir. *p*-alkil kuyruk uzunluğunun organogel oluşumu üzerinde etkisi olduğu bulunmuştur.

Katılaştırma yoluyla organogellerin oluşumu için ısıtma-soğutma prosesi gerektiğinden çevresel uygulamalarda yağın uzaklaştırılması zorlaşır. Jellerin kurutulmasıyla yüksek yüzey alanlı nano-fiber ve gözenekli adsorbanlar elde edilebilir ve aynı amaç için kullanılabilir. Bu projede, seçilen kuru jeller (kserojeller) için yağ çekme kapasitesi de belirlenmiştir. Jellerin morfolojisi optik mikroskop ile incelenmiştir.



**ANAHTAR KELİMELER:** Düşük molekül kütleli organojelleştiriciler, Bis-amidler, Organojeller, Öz-toparlanma, Faz seçici organojelleşme, katılaştırıcılar, Nano-fiber ve gözenekli adsorbanlar olarak kserojeller, Optik mikroskobi

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# LIST OF ABBREVIATIONS AND SYMBOLS

| | |
|---|---|
| **3D** | : Three dimensional |
| **ACN** | : Acetonitrile |
| **AIE** | : Akaike Information Criteria |
| **ALS** | : Molecules with aromatic, linking, and steroidal parts |
| **$^{13}$C-NMR** | : Carbon-13 nuclear magnetic resonance |
| **°C** | : Degree celsius |
| **CAB** | : 3-β-cholesteryl-4-(2-anthryloxy)butanoate |
| **Cbz** | : Carboxybenzyl |
| **$CDCl_3$** | : Deuterated chloroform |
| **$cm^{-1}$** | : Wavenumber |
| **CNTs** | : Carbon nanotubes |
| **CT** | : Charge-transfer |
| **d** | : Doublet |
| **Da** | : Dalton |
| **DNA** | : Deoxyribonucleic acid |
| **E-L** | : Ethyl Laurate |
| **FT-IR** | : Fourier Transform Infrared Spectroscopy |
| **g** | : Gram |
| **$^{1}$H-NMR** | : Proton nuclear magnetic resonance |
| **ID** | : Identification |
| **İe** | : Electrostatic interactions |
| **IPM** | : Isopropyl myristate |
| **IPP** | : Isopropyl palmitate |
| **L-A** | : Linalyl acetate |
| **LMOGs** | : Low molecular-mass organic gelators |
| **LMWGs** | : Low molecular weight organagelators |
| **M** | : Metal |
| **m** | : Multiplet |
| **mgc** | : Minimum gelation concentration |
| **MHz** | : Megahertz |
| **mL** | : Milliliter |

| | |
|---|---|
| **mm** | : milimeter |
| **MWCNTs** | : Multiwalled carbon nanotubes |
| **NBP** | : n-Butyl Palmitate |
| **NMR** | : Nuclear magnetic resonance |
| **O** | : Oxygen |
| ***p*** | : Para |
| **PBA** | : Phenylboronic acid |
| **PG** | : Partial gel |
| **ppm** | : Parts per million (NMR) |
| **ppt** | : Precipitate |
| **q** | : Quartet |
| **RT** | : Room temperature |
| **s** | : Singlet |
| **SEM** | : Scanning electron microscope |
| **Sol** | : Solution |
| **TCM** | : Chloroform |
| **TEM** | : Transmission electron microscopy |
| **USP** | : The United State Pharmacopoeia |
| **UV-Visible** | : Ultraviolet–Visible spectroscopy |
| **X** | : Halogens |

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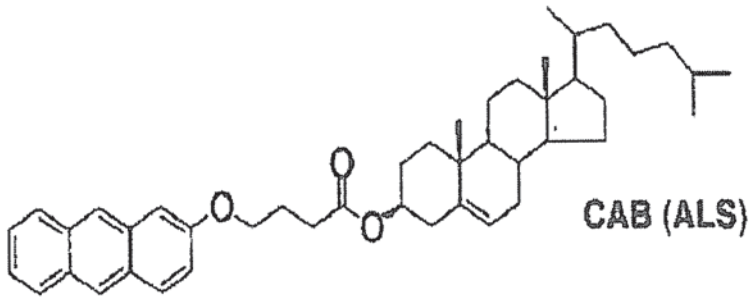
# 1. INTRODUCTION

## 1.1 Development of Low Molecular Weight Organogelators

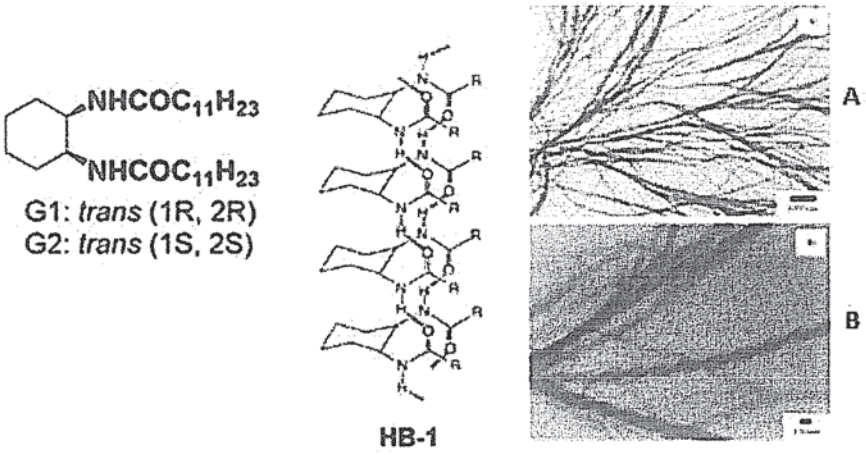
Low molecular weight organogelators (LMWO) are a member of low molecular weight organic molecules that can gel organic solvents at low concentrations. According to D. Jordan Llyod in 1926, 'recognizing the colloidal state as a gel is much easier than it is defined'. Organogels with dimensions of 300-1000 Da are very small macromolecular gels.(P. Terech and R.G. Weiss, 1997)

Organogel studies began in 1987 when C. Y. Lin and his coworker observed that 3-β-cholesteryl-4-(2-anthryloxy) butanoate (CAB, Scheme 1.1) forms gel structure in a wide variety of organic liquids during the photochemical investigation.




**Scheme 1.1.** The structure of CAB molecule

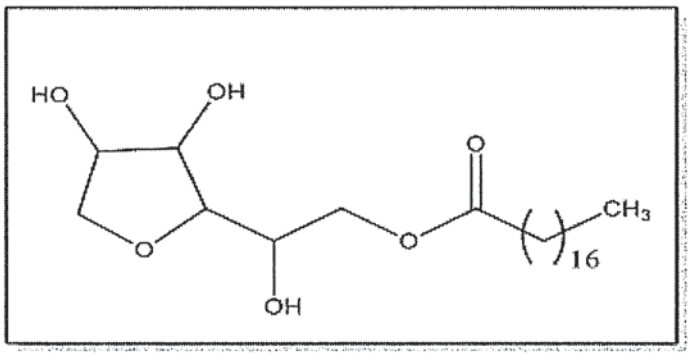
Bis amide organogels first reported by Hanabusa et al. in 1996. They have developed many interesting gelling agents based on amide functionalities. They synthesized G1 and G2 derived from a chiral diamine molecules (trans-1,2-cyclohexyldiamine) (Scheme 1.2) having intermolecular H-bonding part and long alkyl chain part.




**Scheme 1.2.** Amide based gelators G1 and G2, their H-bonding group HB-1 and TEM images of G1-acetonitrile gel (1 mM G1), magnification: (A) 7000; (B) 30000.

P. Terech and his coworker (1997) have researched on fatty acids, anthryl group and streoid derivates of LMOGs and their gelling properties. They found that in fatty acids, "*the molecular packing arrangements of gelators in gel strands and in neat crystalline phases should not be assumed to be the same*"; many gelators are polymorphous even as neat solids.

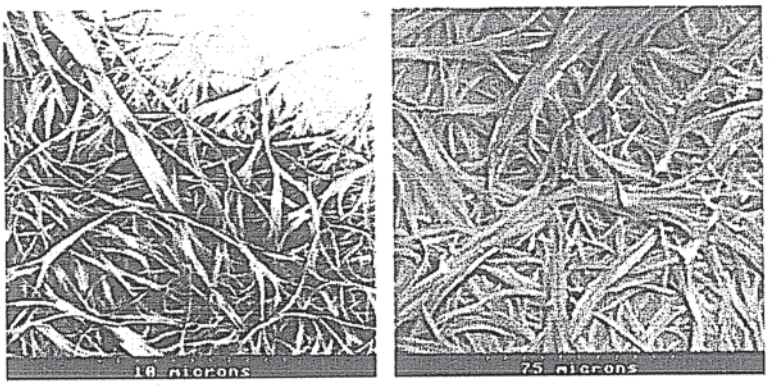
S. Murdan and his coworkers (1999) have synthesized sorbitan monostearate molecule (Scheme 1.3) as a gelator. They achieved gelation in solvents like hexadecane isopropyl mistrate and corn oil and defined the gel structure as an opaque, semi-solid and thermally reversible.




**Scheme 1.3.** The structure of sorbitan monostearate

Hanabusa and his coworkers (1999) investigated the gelation ability of 2-amino-2-phenyl ethanol and they found that a chiral compound containing multiplex H-bonding parts results in the formation of large chiral aggregates, which then accure and become mixed as a result physical gelation occurs.

Bhattacharya and his coworkers (2001) have synthesized a simple aminoacid derivative, N-lauroyl-L-alanine and observed phase selective gelation in a two-phase mixture of water and oil (either commerical fuel or pure organic solvent). They have provided molecular level insights into the process of gelation by SEM and FT-IR (Figure 1.1).

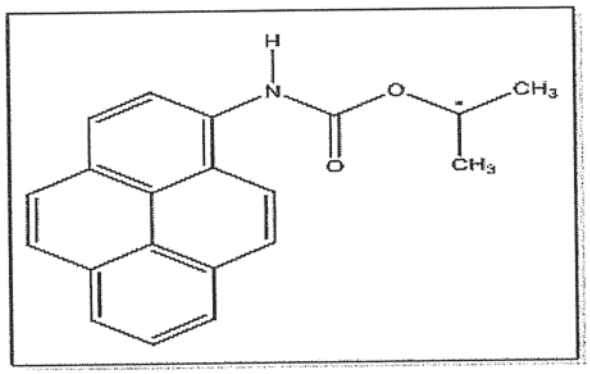



A B

**Figure 1.1.** SEM of gels of (A) n-heptane and (B) toluene with N-lauroyl-L-alanine

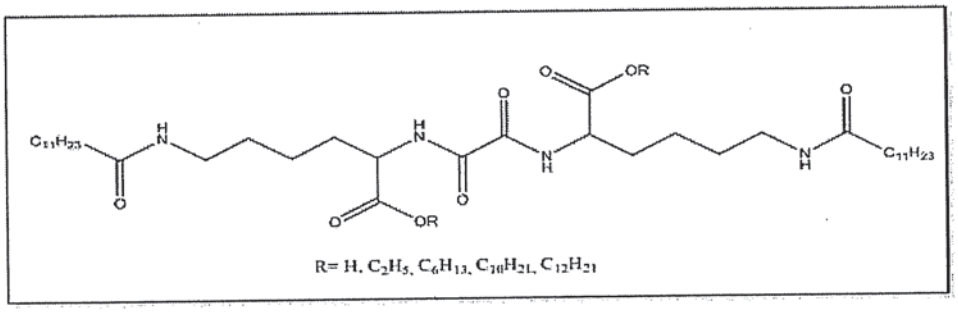
Tomioka and his coworkers (2001) have obtained didodecanoylamides of α,ω-alkylidenediamines as organogelators. They have studied self-assemble into microscopic structures through specific van der Waals interactions, H-bonding, which were the basic interactions for the gelation of organic liquids. They have observed that the chain length of the diamine group was effective on the gel formation.

Maitra and his coworkers (2001) have synthesized 1-pyrene-based organogelators. In their study, a chiral molecule shown in Scheme 1.4 was found to be an organogelator forming a helical gel structure.



**Scheme 1.4.** The structure of 1- pyrene based chiral organogelator

Suzuki and his coworkers (2003) have investigated a new type of bis-amide organogelators linked by an oxalyl amide (Scheme 1.5). They found that the compounds have strong organogelation capabilities and their cyclohexane gels showed superior thermal stabilities. They proved the presence of hydrogen bonding in gel formation by NMR and FT-IR.




**Scheme 1.5.** Chemical structures of a series of oxalyl amide derivatives.

Brosse and his coworkers (2004) have obtained a new member of credible aminoacid-type organogelators. They found that the organogelators with the inclusion of a benzyl or an isopropyl group allowed the gelation of nonpolar solvents at very low concentrations (<2wt%) and the formation of thermostable organogels.

Leroux and his coworkers (2005) have synthesized compounds based on L-alanine. They have observed the ability of gelation in herbal oils to be used in pharmaceutical industry. They also demonstrated that these gels can be used in drug delivery systems.

Lu and his coworkers (2006) have obtained benzoic acid hydrazine-based novel organogelators to investigate the interactions between gelator molecules during gel formation. UV-Visible and IR methods have been used to explain the mechanism of gel formation. They also investigated 3D-gel structure by SEM analysis.

Smith and his coworkers (2007) have synthesized new LMOGs containing carbamate and urea groups to examine gelation properties in organic solvents like toluene and cyclohexane. They found a fibrous structure of these oganogels proved by SEM analysis.

Chow and his coworkers (2007) have synthesized new molecules with 3,5-diaminebenzoate linked esters containing α- or β-aminoacid and aromatic groups, and investigated gel properties in aromatic solvents. In this study, it was observed that the additional aromatic rings in the Cbz- and aromatic-containing ester parts extremely improved the gelation properties of the resulting organogelators in aromatic solvents. They have investigated the gelation mechanism by FT-IR and CD (circular dichroism) spectroscopy. According to the results of spectroscopic studies, the main driving forces for gelation are H-bonding and π–π aromatic stacking interactions.

Sanders and his coworker (2007) synthesized chiral *N,N'* dimethylnapthalinediimide based aminoacid derivatives and investigated their organogelation properties. They found creativing helix structure in nonpolar solvents formed by hydrogen bonding. It was also found that the chirality of the helix structure is governed by the aminoacid functionality.

Lim and his coworkers (2008) gelated terpenes in propylene glycol and dibutyllauroylglutamide. They investigated physicochemical properties of the terpene gels and used them in drug carrier systems. They showed the gelation of these terpenes as represented in Figure 1.2.

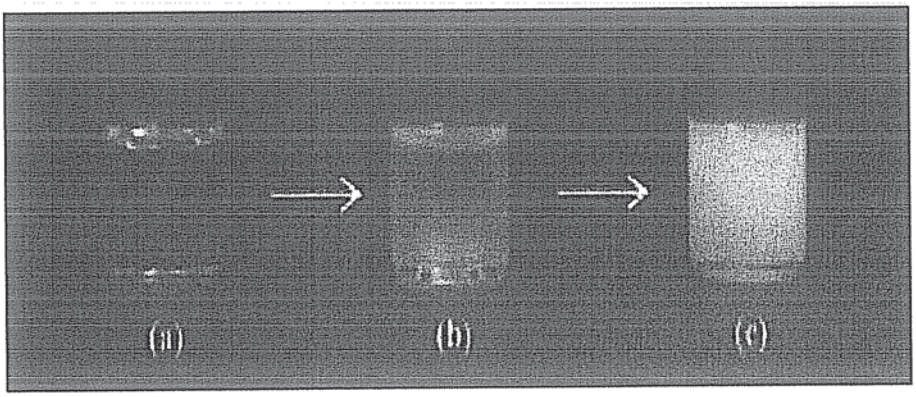
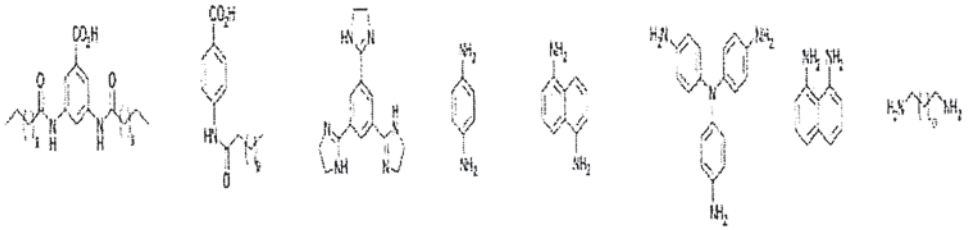



**Figure 1.2.** Gelation process (a) clear solution after heating; (b) uniform, cloudy suspension upon cooling and standing; (c) white gel upon further standing.

Hong and his colleagues examined (2008) organogelators of self-assembled aromatic amines and amphiphilic groups (Scheme 1.6) that have sufficient aromatic stacking and H-bonding interactions in non-aromatic hydrocarbon solvents.



**Scheme 1.6.** The structures of organogeltors.

Das et al. (2008) synthesized dipeptide-based low molecular weight organogelators (LMWOGs) and used them (in the form of wet and dry gels) to remove toxic dyes such as cystal violet, rhodamine 6G from water (Figure 1.3). They also used FT-IR and temperature dependent NMR methods to provide the gelation mechanism.

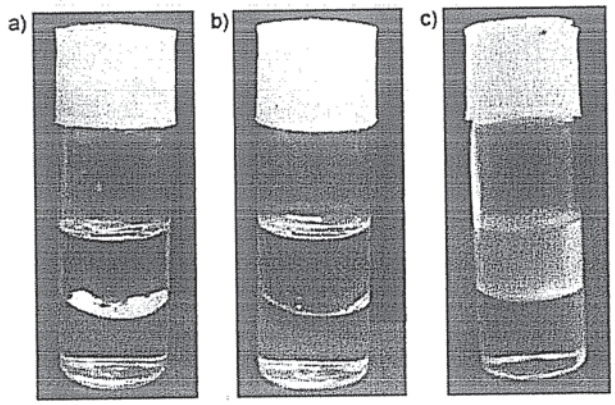



**Figure 1.3.** a) 1 mL toluene and 1 mL water together with 10 mg of gelator. b) Gelator was dissolved by heating. c) Selective gelation of toluene layer by gelator at RT.

Luo and his coworkers (2009) proved that LMWOGs based on monochain derivatives of ethylenediamine are influential gelators in organic liquids (Figure 1.4). They determined the gel structure in nonvolatile toluene and carbontetrachloride by SEM analysis, and the presence of H-bonding by FT-IR. FT-IR studies have shown that intermolecular H-bonds between adjacent molecules are the crucial factor in the process of organogelation.

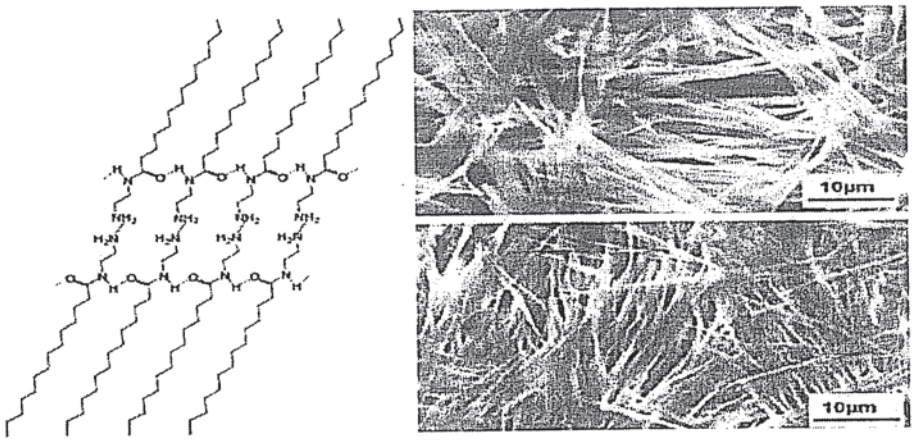



**Figure 1.4.** The structure of aggregates in organogel formation and SEM images of xerogels

Lin and his coworkers (2010) have synthesized a chiral organogelator that can be self-assembled and racemized in nonpolar solvents. They have observed formation of fibrils that are able to gelate the solvent by SEM (scanning electron microscopy) and H-bonding interactions among the peptide head groups of neighbouring organogelator molecules by $^{1}H$ NMR spectroscopy.

John and coworkers (2010) synthesized a novel class of sugar-based gelators for oil spill remediation. They demonstrated the recovery of oil and reuse of the gelator for the first time in the model system. In their study, gelators were efficient to remove the oil part selectively from oil–water mixtures (Figure 1.5).

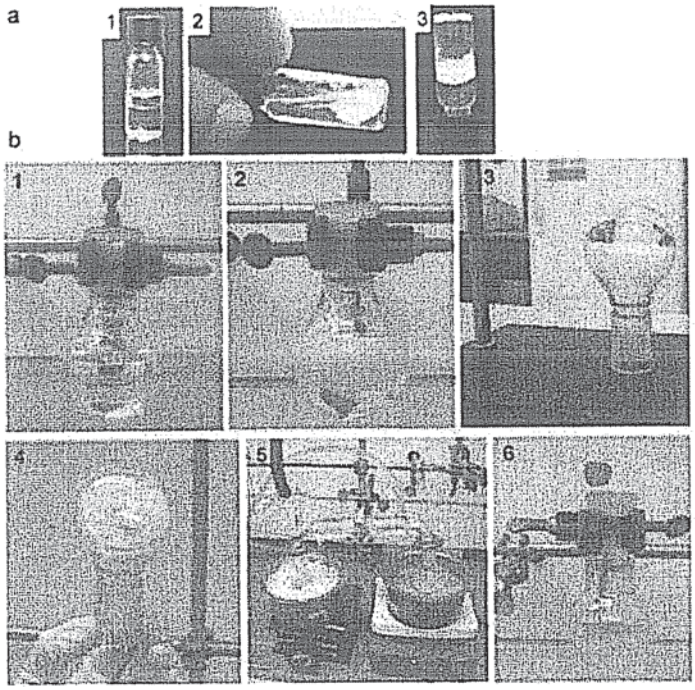



**Figure 1.5.** Phase-selective gelation and diesel recovery from a two phase system.

Sundararajan and his coworker (2011) synthesized biscarbamate-based molecule (C12) which has two H-bonding parts symmetrically joined to n-dodecyl side chains. They obtained non-chiral organogelator that forms empty fibers and encapsulates silver nanoparticles (SNP) and a dye molecule. In addition, they gelled the compounds in the form of nanotube shape and fiber structure in benzonitrile (Figure 1.6).

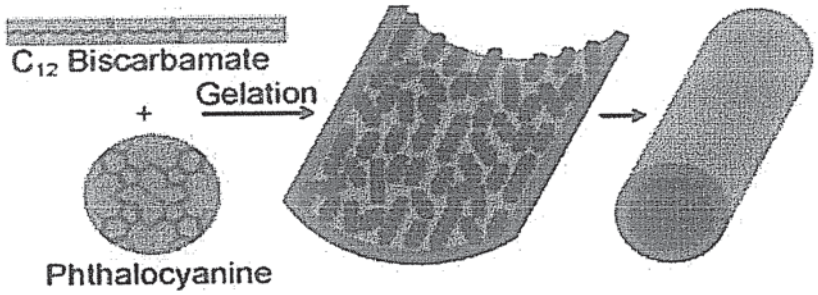



**Figure 1.6.** Nanotube shape of biscarbamates in benzonitrile.

Chen et al. (2011) described the synthesis of LMWOGs including 2-substituted antraquinone and a hydrazine subunit. They investigated the chemical structure property relationships with respect to their gelation characteristisc and found exceptional thermal stability of toluene gels and ultrasound promotion on gelation. Furthermore they concluded that the hydrazide-based organogelators indicated phase selective gelation of aromatic solvents in the presence of water (Figure 1.7).

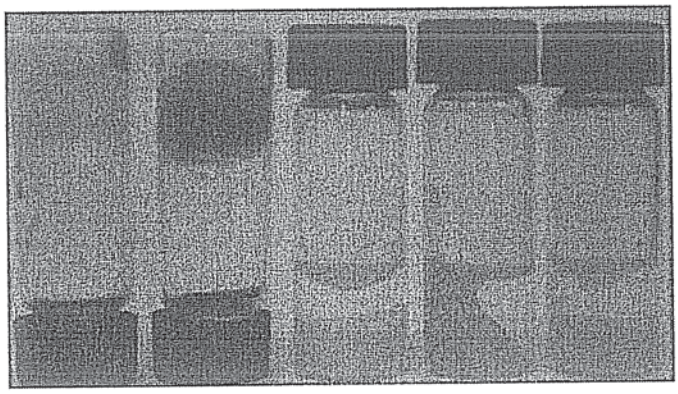
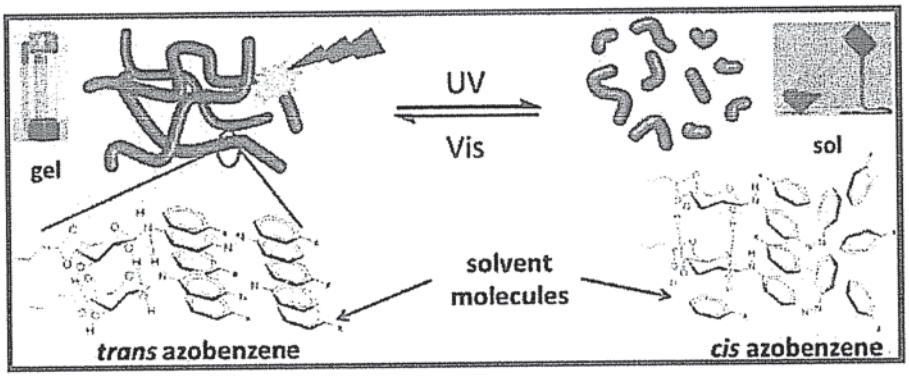


**Figure 1.7.** Phase selective gelators in presence of water (1/1 vol %). Sequential: toluene, aniline, 1,2-dichlorobenzene, chlorobenzene, chloroform.

Pourjavadi and his coworkers (2012) synthesized new carbon-nanotube-based (CNT) organogels for oil recovery. The oil-absorbent including CNTs have displayed high enlargement capacity in oil and organic solvents compared with that without CNTs. They also reported CNT-based organogels could be utilized as a good oil-absorbent for environmental preservation and oil recovery.

Minakuchi et al. (2012) have synthesized organo-gelatinizing molecules containing amino acids, gluconic acid and long alkyl chains and have gel in some organic solvents, water, ionic-liquids, biodiesel and olie oil. They have stated that elecrochemical applications of gels, especially those obtained from ionic liquids and other gels may be used in biochemistry fuel and environmental applications.

Rajaganesh et. al. (2012) stated that N-glycosylazobenzene structures are photoresponsive supergelators due to cis-trans isomerism resulting from the sensitivity to light (Scheme 1.7). They reported that the obtained gels could be used to purify water from toxic aromatic solvents because of selective gelation of aromatic solvents.




**Scheme 1.7.** N-glycosylazobenzene having selective gelation of aromatic solvents

Chung and his coworkers (2013) synthesized biscalixarene framework with short alkyl chains beginning with the main calix[4]arene. They reported the occuring product (biscalix[4]arene) was able to form organogels in several alcoholic solvents. Besides they indicated that this gel exhibited phase selective gelation property that is promising for oil spill recovery (Figure 1.8).

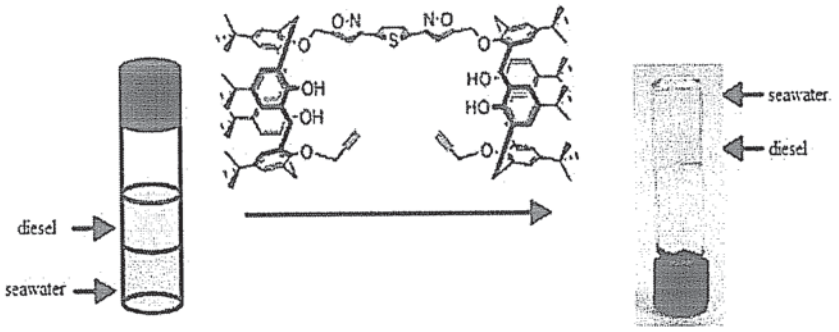



**Figure 1.8.** Phase selective gelation of biscalix[4]arene

Hu and his coworkers (2013) found that two-component charge-transfer (CT) interaction induced organogel formation occured between 18β-glycyrrhetinic acid appended pyrene donor and 2,4,7-trinitrofluorenone acceptor. UV–vis, fluorescence, mass spectrometry and $^{1}$H NMR experiments (Figure 1.9) have shown that the main driving force of the CT gel formation is the charge transfer interaction.

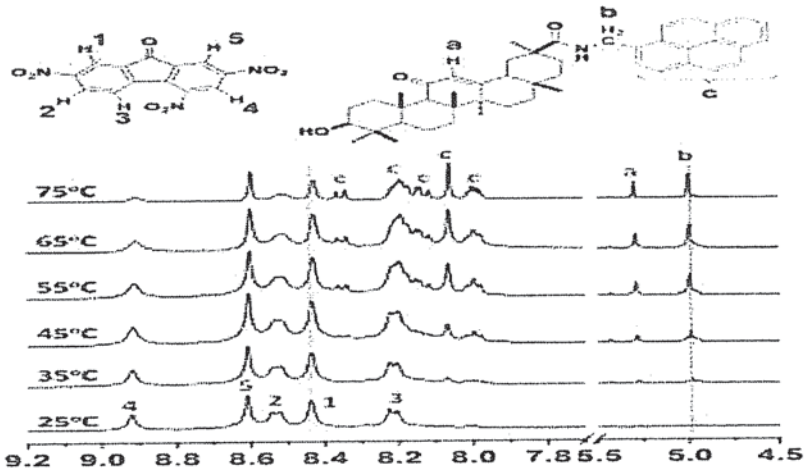
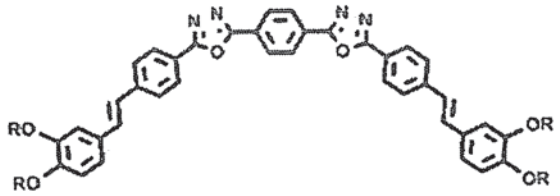



**Figure 1.9.** Variable temperature $^{1}$H NMR (400 MHz) of CT gel

Aneesh and his coworkers (2014) have synthesized a series of luminescent 1,3,4-oxadiazole molecules (Scheme 1.8). They have observed very strong supergelating character for molecules exhibiting super structures in liquid crystalline. This result is surprising because molecules do not possess any H-bonding motifs.




OXD1: R = $CH_3$ OXD4: R = $C_4H_9$

OXD6: R = $C_6H_{13}$ OXD8: R = $C_8H_{17}$

OXD10: R = $C_{10}H_{21}$ OXD12: R = $C_{12}H_{25}$

**Scheme 1.8.** Oxadiazole-based stilbene molecules chemical structure

Feng et al. (2014) obtained $C_2$-symmetrical benzene compounds having selective gelation against aromatic solvents and tested the gelation in water-oil mixtures (Figure 1.10). This $C_2$-based organic gelator presenting phase selective gelation has tremendous applications for the removal of oil spill. The compounds formed gel structure in dimethylbenzene layer and the water layer have remained intact in liquid state.

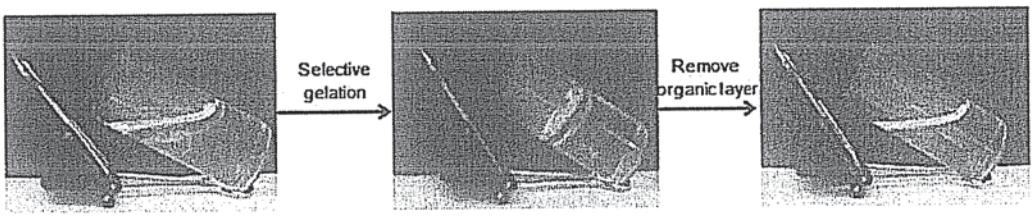



**Figure 1.10.** Selective organogel formation from oil/water of 1,4-Bi(phenylalanine-ethylene glycol monohexyl ether)-benzene (PEB)

Löfman and his coworkers (2015) studied the nucleation-development of several gelating and non-gelating bile acid aminoamide systems. They stated that the results of the dynamics at micro- and macroscale allowing a structure for the macroscopic regulations of spherulitic formation of a fibre-like non-gelating or gelating models

López and his coworkers (2015) described a novel self-assembled organogel system based on 5-(4-nonylphenyl)-7-azaindole, possessing an aggregation-induced emission phenomenon (AIE). They reported that the self-assembly in 5-(4-

nonylphenyl)-7-azaindole-cyclohexane gels resulted in a supramolecular soft matter through van der Waals interactions between long alkyl groups.

Pang and his coworkers (2015) have designed and characterized a naphthalimide-based fluorescent gelator containing an alkenyl group. They reported an in situ and instant precipitate-to-gel formation triggered by ultrasound at room temperature. In their study, the gelation process in n-propanol was proved by absorption, fluorescence IR spectroscopy and scanning electron microscopy (SEM) (Figure 1.11).

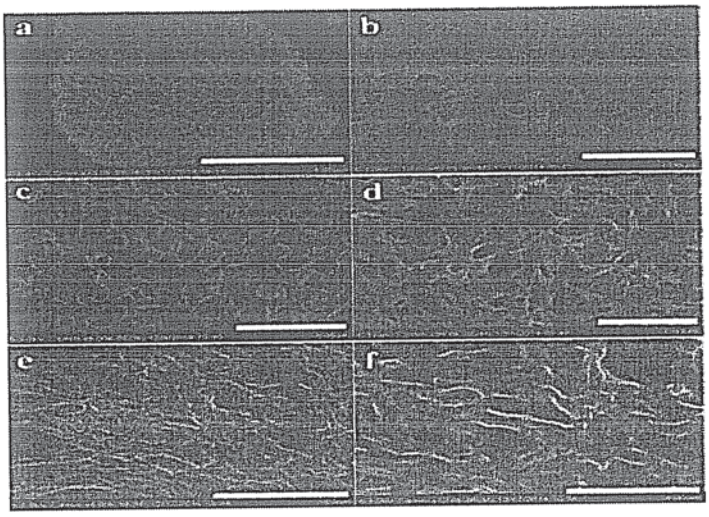



**Figure 1.11.** SEM images of naphthaline based xerogels

Xu and his coworkers (2015) have designed and synthesized PBA (phenylboronic acid) based LMWOGs (Figure 1.12), which gelated solvents efficiently at relatively low concentrations. These organogels showed nanofibers, thin films and microspheres piled with nanofibers and had good performance in pH-response and glucose-response. They proved the molecular interactions by IR spectroscopy and $^{1}$H-NMR measurements and concluded that together with H-bonding van der Waals and π-π stacking interactions have the main contribution in the gelation process and the formation of aggregates.

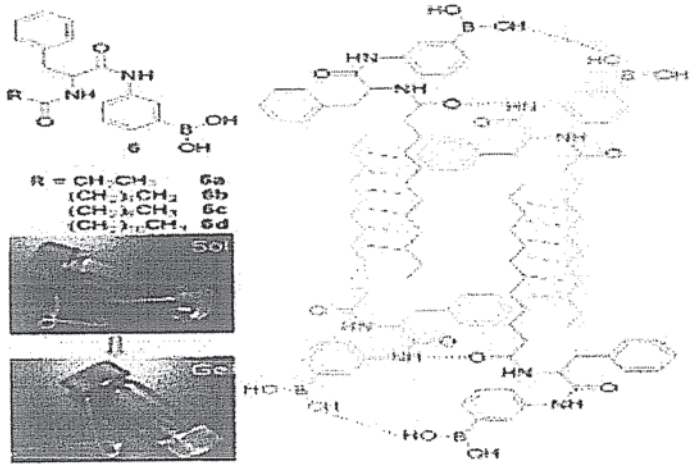
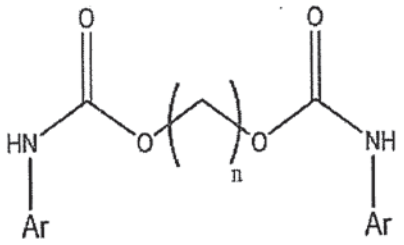


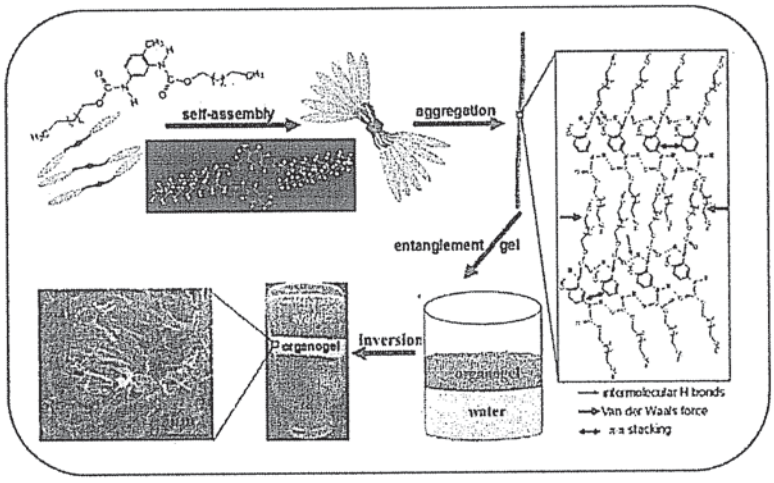
**Figure 1.12.** The chemical structure of gelators; interactions between gelator molecules and sol-gel transition of organogels.

Demir-Ordu and her coworkers (2015) synthesized bis-carbamate-based LMWOGs (Scheme 1.9) that are able to immobilize organic solvents and they described the effect of the structure properties on the gelation ability. They reported that the driving force for self-association and gelation ability of the compounds are the H-bonding of carbamate units, the van der Waals interactions of *p*-alkoxy tails and π-π interactions of phenyl rings evidenced by the results from FT-IR and NMR spectroscopies. They also found that for *p*-alkoxyphenyl derivatives, the methylene units with even and odd numbers in the spacer are significant for organogel formation. They investigated temperature effect on the gel formation for all compounds. The formation of stable gels was achieved by lowering the gelation temperature along with the extension of the *p*-alkyl chain. Furthermore they investigated thermal stability of the gels by dropping ball experiments and DSC. Morphological structure of xerogels were investigated by SEM. Besides, *para*-alkoxyphenyl derivatives were found to have good organogelation properties for vegetable oils and esters.




**Scheme 1.9.** Chemical structures of the bis-carbamate compounds.

Wang and his coworker (2017) have synthesized biscarbamate-based supramolecular organogelators with different lengths of side alkyl chains. Notably, they reported the gelators with intermediate length of alkyl side chains possess the best gelating abilities (Scheme 1.10). These phase-selective organogels have self-assembled 3D network structures in several types of organic solvents and oils from oil/water mixtures, like petroleum products (crude oil, diesel, gasoline), cyclohexane, hexane. The intermolecular self-assembly are formed through hydrogen bonding, π-π stacking and van der Waals interactions, etc. Furthermore, they reported the phase selective organogel formation for organic solvents and oils showing high oil removal and oil retention rates.




**Scheme 1.10.** Schematic representation of formation process of the gel networks.

## 1.2 Theory

### 1.2.1 What Is Gel?

150 years ago Jordan Lloyd described gels as 'colloidal condition'. According to Flory gels are not in colloid form. Nowadays, gels are solid and like-jelly unless the external mechanical effects.

Gel can not be defined precisely, but from a topological standpoint, gels can be defined as dilute mixtures containing at least two components. In a gel system these components form a separate continuous phase. (Flory, 1974)

A simple working definition of the term 'gel' is a soft, solid or solid-like material, which contains both solid and liquid components. During gel formation the solid component immobilises the liquid component and prevents the liquid from flowing, via surface tension.(Savale, 2016)

According to The United State Pharmacopoeia (USP) definition, gels are semisolids and either suspensions of small inorganic particles or large organic molecules interpenetrating with liquid. (Bhardwaj et al., 2012)

Organogels are semi-solid semi-organic liquid phase assemblies formed by immobilization of an organic liquid by a three-dimensional network of intercalated gelator fibers. In spite of the majority of liquid composition, these systems demonstrate the solid-like appearance and rheological behaviour. (Vintiloiu and Leroux, 2008)

The gelator fibers interact to form a three-dimensional network that holds the solvent, and at the macroscopic level, this formation results in gel formation. (Chen et al., 2008)

### 1.2.2 Types of Gels

Gels are generally classified into two types: chemical and physical gels. Physical linkages in gels might include van der Waals, dipole-dipole interactions,

properties of crystallinity, multiple helices etc. Factors such as time, pressure, and temperature affect the number of physical cross links in a system. Physical gels are thermoreversible; that is, the gel-forming bonds break over the sol-gel transition temperature and a solution forms. In the opposite case, if the gel is cooled under the sol-gel transition temperature, it can be converted into a gel again. A special class of physical gels is low molecular weight organogels. These organogelators create a 3D network by self-assembly through noncovalent interactions such as H-bonding, π-π stacking, van der Waals interactions (Sperling, 2006).

Gels are classified into two classes according to the solvent used in gelation; hydrogels and organogels (Sri, et al., 2012).

#### 1.2.2.1 Hydrogels

Hydrogels are crosslinked polymers with the capability to swell in an aqueous medium. Crosslinking can be formed chemically or physically. Hydrogels include various chemical structures and cross-linking methods, for pharmaceutical and biomedical preparations have been prepared for various applications. Hydrogel can respond to environmental alters such as pH, temperature and swelling medium by modification its size or shape (Siepmann et al., 2012).

Hydrogels can be divided into two groups depending on the type of crosslinking reaction. Physical hydrogels are formed due to the physical interactions among the polymeric chains. On the other hand permanent hydrogels are formed by crosslinking reactions including the formation of covalent bonds (Hoffman, 2002).

#### 1.2.2.2 Organogels

Organogels are semisolid systems which include gelator substance and a non-polar or a polar solvent. The formation of the 3D network structure occurs by noncovalent interactions such as hydrogen bonding, van der Waals interactions, π-π stacking, coordination etc. between gelator molecules. The organic phase is entrapped inside a 3D network. The organogels can be converted from gel to solution

by the action of heat and they can return to gel structure again when they are cooled. (Gupta et al., 2014)

Organogels can be considered as a thermodynamically stable semi-solid system that are usually viscoelastic (Sahoo et al., 2011).

According to weight of gelator molecule, organogels are divided by two as low molecular weight organogelators (LMOGs) and polymeric gelators (Vintiloiu and Leroux, 2008). (Figure 1.13)

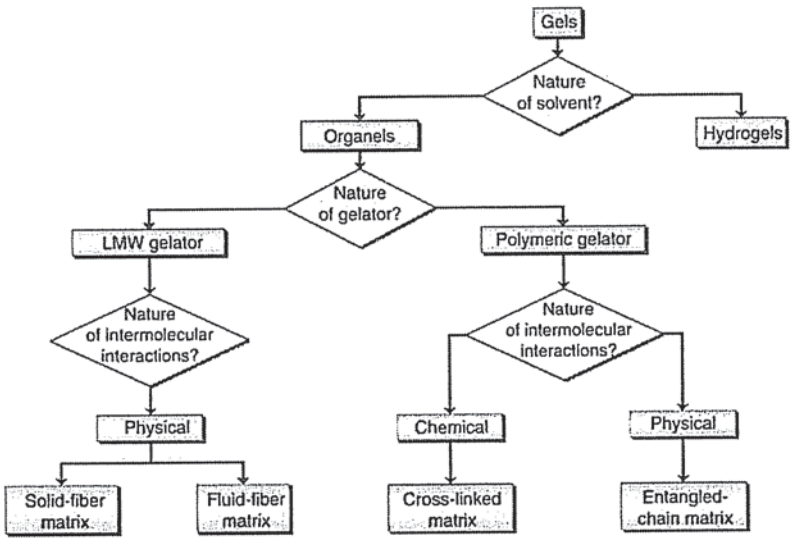



**Figure 1.13.** Schematic representation of organogels classification (Vintiloiu and Leroux, 2008)

#### 1.2.2.2.1 Low molecular weight organogelators (LMOGs)

Low molecular weight organogelators are low molecular weight compounds, which have the ability to immobilize nonpolar solvents, even when used in small concentrations (< 2%) (Toro-Vazquez, et al., 2007)

Organogels are the form of gels in which solvent molecules entrapped in three dimensional networks by weak intermolecular interactions. The main characteristic features of low molecular weight organogelators is thermo-reversible self-assembly and dis-assembly process (Liu and Ma, 2011).

In gel-phase materials, a very small amount of organic gelator, occasionally as little as 0.1% w/v, can 'immobilise' the solvent and form a self-supporting gel (Smith, 2007).

The propensity of a low molecular weight molecule to form LMOGs is classified by its minimum gelation concentration (mgc). According to Lin and Weiss (1987) "the mgc is the lowest possible gelator concentration needed to form a stable gel" (Lin and Weiss, 1987).

The important factor affecting the formation of the low molecular weight organogels (Hoare and Kohane, 2008);

- Fiber formation by control of an anisotropic growth process
- Intertwining of the aggregates in a 3D network
- Prevention of crystallization

#### 1.2.2.2.2 Polymeric organogelators

Polymeric organogelators have organogelation properties even at very low concentrations. Polymeric organogelators gain their geling ability by modifying the chemical structure of the polymer backbone. (Pawar et al., 2014)

The gels improved by polymeric organogelators usually have lower gel-sol transition temperature and in some degree higher gel strength when compared with organogel improved with LMWOs. (Pawar et al., 2014)

Polymer organogelators' gelation properties are significantly influenced by low molecular weight gelator and polymeric backbone structures (Suzuki and Hanabusa, 2010).

### 1.2.3 Conditions required for gelation

There are three important criteria required for gelation:

1. Molecule must be partially soluble in the solvent. Thus, it dissolves when the heat is applied and it gels when it is cooled.
2. Molecule must not be partially soluble in the solvent. If the solubility is very low, when heat is given, dissolving is not completed and gelation is not observed.
3. Molecule self-assembly can interact with noncovalent interaction (H-bond, π-π interaction and hydrophobic interaction). H-bonding is the most important factor for gel structure constituent(Smith, 2007)

### 1.2.4 Types of intermolecular interactions

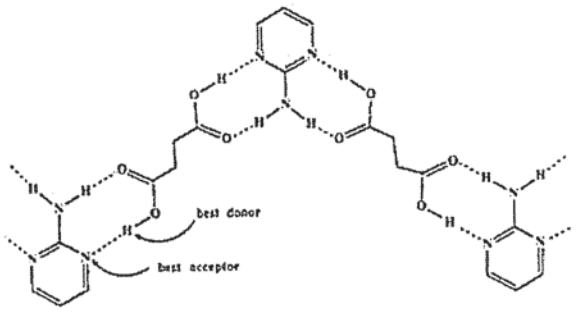
Intermolecular interactions have been found to influence the gelation process. Intermolecular interactions between gelator molecules can be London dispersion forces, ionic-ionic, dipole-dipole, hydrogen bonding, van der Waals and π-π stacking interactions (Vintiloiu and Leroux, 2008).

Supramolecular chemistry is based upon intermolecular interactions (hydrogen bonding, π-π stacking, van der Waals interactions). In supramolecular chemistry the building blocks are reversibly held by intermolecular forces resulting in non-covalent assemblies. The term 'non-covalent' contains an enormous range of intermolecular interactions, which on the other hand originate from only a few attractive and repulsive forces which represented in the order of decreasing strength. (Lehn, 1969)

1. Electrostatic interactions
2. Hydrogen bonding
3. π-π stacking
4. van der Waals forces

### 1.2.4.1 Hydrogen bonding

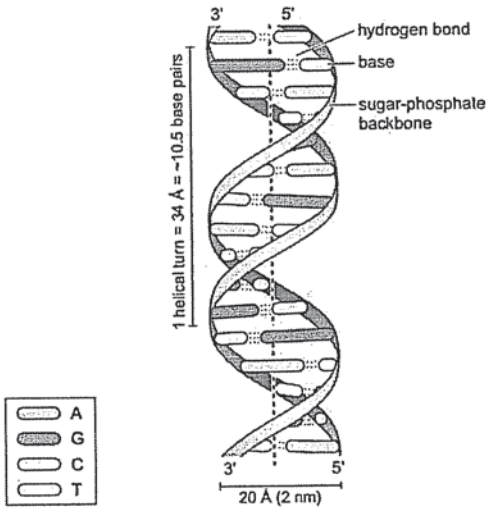
According the IUPAC, "hydrogen bond is an attractive interaction between a hydrogen and an atom, X which is more electronegative than hydrogen" (Scheme 1.11). (Arunan et al., 2004)




**Scheme 1.11.** Hydrogen bond formation (Etter, 1990)

Hydrogen bonding is formed when a highly electronegative atom comes close to a hydrogen atom attached to another electronegative atom. In biochemical systems oxygen (3.44) and nitrogen (3.04) are the most electronegative atoms. A tendency in electronegativity throughout a covalent bond results in the more electronegative ions pulling shared electrons towards themselves resulting in an electric dipole throughout the bond. (Brandeis Uni., 2007)

In the history of structural biology H-bonds have played a significant role. DNA structure, protein α-helices and β-sheets are described based largely on the hydrogen bonds (Brandeis Uni., 2007). (Scheme 1.12)

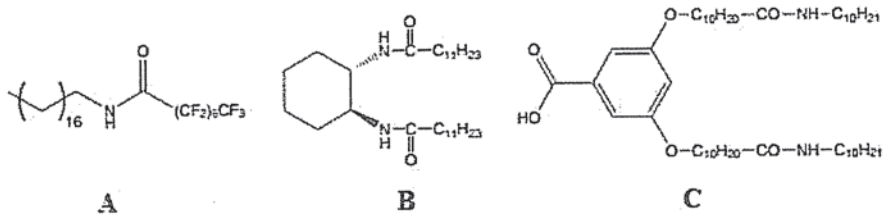



**Scheme 1.12.** Schematic model of the DNA structure (Dickerson, 1983)

Intermolecular H-bonding among N-H and C=O plays a significant role in gel formation of LMOGs based on amides, amino acids, ureas and urethanes. Compound A (Scheme 1.13) is an example of *N*-alkyl peruoroalkanamides which forms gels in a few organic solvents including aliphatic hydrocarbons, alcohols, toluene (Fages et al., 2005).

Another example is compound B (Scheme 1.13) to gelate various solvents like hydrocarbons, alcohols, ketones, esters and mineral oil. Compound B enable the hydrogen bonding between the amide groups of adjacent molecules and van der Waals interaction of the long alkyl chains (Jung and Hanabusa, 2000).

Aromatic bisamide, compound C (Scheme 1.13) is capable of forming gels in aromatic solvents like benzene, toluene and *p*-xylene, but not in aliphatic hexane due to insolubility. The compound C (Scheme 1.13) without the presence amide groups are not a gelating molecule for aromatic solvents indicating that hydrogen bonding between the amide groups is crucial for gel formation (Schmidt et al., 2003).




**Scheme 1.13.** LMOGs based on amides

### 1.2.4.2 $\pi - \pi$ Interaction

$\pi$-$\pi$ interaction is a noncovalent interaction that has a small but significant role in the formation of organic molecules. This interaction sights between two aromatic rings or between a functional group and an aromatic ring. The functional group has a lone pair electron and this electron pair plays as an electron donor, meantime the aromatic ring plays as an acceptor (Hitomi et al., 2007).

According to Hunter interactions that occur in a parallel face-to-face orientation between the $\pi$-clouds of aromatic systems are termed aromatic $\pi$-$\pi$ stacking interactions. This interaction takes an important role in, self-assembly, supramolecular chemistry, and general host-guest interactions (Figure 1.14) (Waller et al., 2006).

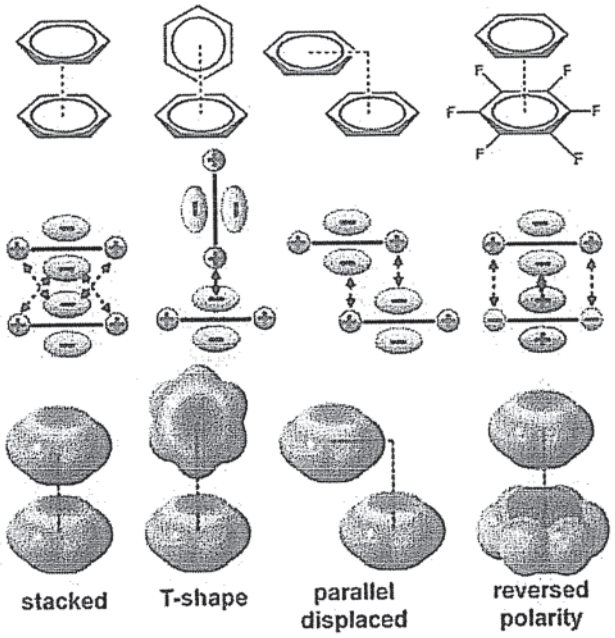



**Figure 1.14.** Geometries, quadrupole moments and ESPs (blue is positive and red is negative) of typical p–p aromatic interactions. (Matthews, Welton and Hunt, 2014)

### 1.2.4.3 van der Waals interactions

van der Waals forces are the combination of the attractive and repulsive electrical forces between atoms and molecules and they can be given as an example for the weak intermolecular forces. These interactions result from fluctuations in charge density of particles. Negative-charged parts of one molecule are repulsed by negative-charged parts of another molecule. On the other hand, positive parts of a molecule attracted to the electrons of another molecule (Helmenstine, 2015).

Intermolecular forces define melting-boiling points, solubility, electrical conductivity, heat conductivity, crystal structure, and hardness of substansces. The electrostatic interactions for uncharged molecules (with no formal charges) are often classified as (Ebbing and Gammon, 2009);

A) Dipole- dipole interactions

B) London forces

### *A) Dipole – Dipole Interactions*

The dipole–dipole force occurs among polar molecules. The dipole-dipole forces result from the attraction between the positive and negative ends of the molecules. However, this attraction is very weak compared to ionic interactions (Ebbing and Gammon, 2009).

### *B) London forces*

London forces ( also called dispersion forces) emerge as the result of the free movement of electrons in an atom or molecule. The charge distribution due to electron density in the atom can change at any time. The formation of more electron density on one side of the atom also changes the distribution of charge on the adjacent atom. Thus, temporary dipoles are formed and new dipoles are formed without the dipoles disappearing. The London forces are the weakest interactions between molecules (Helmenstine, 2016).

London forces become stronger as the molecular weight increases. This is due to the increased polarizability and greater surface area (Ebbing and Gammon, 2009).

## 1.2.5 Gelation process

Studying with the gel is relatively difficult due to its relatively irregular nature and its structural properties. Several experimental methods have been used to examine self-assembly and gelation ability of LMOGs together with morphology, thermotropic and rheological properties of the gels. But the applicability of these techniques is dependent on the structure of the gelator and the solvent molecules(Leivo, 2011).

Dual H-bonding interaction is the major force for gel formation. Besides the hydrogen bonding the van der Waals and $\pi$-$\pi$ stacking also have a strong effect on the molecules' ability to self-assemble into 3D network (Wang et al., 2017).

For aprotic, organic solvents, hydrogen bonding is frequently the most significant force for guiding the self assembly process. Unlike aprotic organic

solvents, for polar protic organic solvents, hydrogen bonding and electrostatic interactions are not as significant. According to Lucas (2001) another important issue is to establish a sensitive balance between hydrophobicity and the hydrophilicity of the gelator molecules. According to Lucas too much solvophobicity causes the gelator molecule to collapse or crystallize. Another situation is the formation of solution due to excessive dissolution of the gelator molecule (Lucas, 2001).

Gelation is usually tested by heating the gelator and solvent mixture and allowing the hot solution to cool to room temperature. This method is called "the inverted test tube method" and that is the simplest and most common method for evaluating the state of the sample. According to the inverted test tube method if the sample does not flow under gravitation it is regarded as a gel (Leivo, 2011).

For gelation, the molecule must have self-assembly capacity so that a three-dimensional fiber structure can form. In order to form a three-dimensional fiber structure, it is first necessary to form single thin fibers in one dimensional. As the fibers entanglement, a 3D structure is formed over time (Figure 1.15).

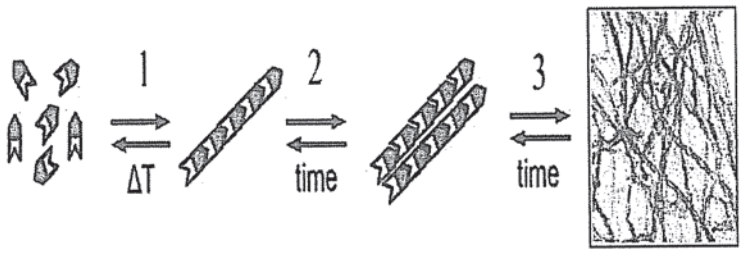



**Figure 1.15.** Schematic representation of the formation of a 3D- network starting form dissolved gelator molecules (Lucas, 2001)

As shown in Figure 1.16, when the hot solution is cooled, the molecules start to condense and three situations are possible:

- Crystal formation, a highly ordered aggregation,
- An amorphous precipitate formation, a random aggregation,
- Gel formation, an aggregation process between the two options. (Maity, 2007)

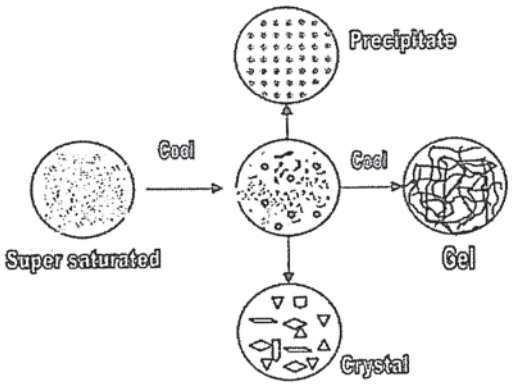



**Figure 1.16.** Schematic representation of aggregation modes (Maity, 2007)

# 2 AIM AND SCOPE OF THE STUDY

In recent years, gels formed by low molecular weight organic compounds with a wide variety of organic liquids have begun to be investigated with increasing interest. Gels formed by low molecular weight organic compounds are being used in many areas. Examples of these areas include drug delivery, cosmetics, sensor systems, phase-selective cleaners.

Phase selective organogelators, have been attracting a lot of attention in water purification and oil-spill recovery (Figure 2.1). These organogelators are preferred because they are cheaper and simpler to use than currently used methods.

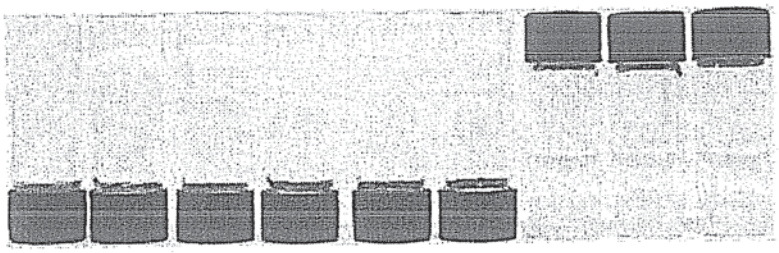


**Figure 2.1.** Phase-selective gelation of aromatic solvents. From left to right: toluene, p-xylene, xylene, mesitylene, p-chlorotoluene, chlorobenzene, bromobenzene, 1,2-dichlorobenzene, and chloroform. (Zhang et. al, 2015)

In our previous study supported by TUBITAK (Demir-Ordu, et al., 2015), it was observed that bis-carbamate based LMWOGs (Scheme 1.9) can gelate organic solvents like toluene, xylene, esters used in pharmaceutical industry like ethyl laurate, n-butyl palmitate, isopropyl myristate and vegetable oils like olive oil, corn oil and sunflower oil. The bis-carbamate molecules possess three different structural parts; two carbamate units that are capable of forming H-bonds, an aryl part substituted by electron donating groups which might increase the strength of π–π stacking and aliphatic spacers of different length that can be involved in van der Waals interactions. The results showed that: (i) the length of alkyl spacer, (ii) the presence of *p*-alkyl or *p*-alkoxy groups and their chain length, (iii) concentration and

(iv) temperature affect the organogelation process. Especially for *p*-alkyl derivatives, the presence of three methylene groups between the carbamate groups has an important role in organogellation. For *p*-alkoxy derivatives, the number of methylene groups must be odd (three and five). Moreover, cryogels were obtained at -18 °C only for *p*-alkyl substituted bis-carbamate derivatives. This was the first result in literature. Unlike the other nano-fibrous gels, the xerogel of hexyl derivative exhibited a porous structure. Mechanism of gelation (the presence of H-bonding, $\pi-\pi$ stacking and van der Waals interactions) was investigated by IR and NMR.

With these results in hand, the main purpose of this study is to obtain bis-amide-based materials that can be used in environmental applications. Bis-amide derivatives are designed due to their better hydrogen-bond formation ability compared to bis-carbamates. These materials obtained in "sorbent" and "solidifier" forms were used in order to remove vegetable/petroleum oil spills from water. In this study, first, new bis-amide derivatives were synthesized and their organogelation behavior were studied in common organic solvents, vegetable oils (olive oil, sunflower oil, nut oil etc.), and petroleum products (gasoline, diesel etc.). The ability of oil spill removal from water was determined by test tube inversion method.

Demir-Ordu et al. (2015) reported that porous material (xerogel) with high surface area was obtained from the cryo gel of *p*-hexyl derivative after drying. Network structures with high surface area and nano-fibers have been obtained for *p*-butoxy and *p*-hexyloxy derivatives. With this result in hand, nano-fibrous and porous sorbents having high surface area could be obtained by drying the gels and used in the removal process since heating-cooling prosess is required for the formation of organogels via solidification which makes the removal of oil difficult in environmental applications. In this study, oil removal capacity of the sorbents were also determined for selected xerogels. The morphology of sorbents were examined by optical microscopy.

To summarize, the purposes of this work were:

-to synthesize *p*-alkyl substituted aryl bis-amides

-to study organogelation abilities of bis-amide derivatives by examining the influence of the length of the *p*-alkyl substitution on gelation.

-to observe phase selective gelation nature of bis-amide derivatives in water-organic solvent mixtures.

-to find oil removal capacity of selected xerogels

It is known that variations in the structures allow us to understand the basis of the relation between self-assembly/gel properties and molecular structure and may give an opportunity to develop new nano fibrillar materials. In literature, phase selectivity and removal of organic pollutants from water by low molecular weight organogelators is a very brandnew topic. There are a few number of publications in recent literature and they include only a few trials for a few solvents and derivatives. Also the oil removal capacity has not been examined in these studies. Besides, there is no report in the literature regarding oil removal by sorbents (xerogels). This study will also contribute the potential environmental applications in many aspects.

# 3 MATERIALS AND METHODS

$^{1}$H-NMR and $^{13}$C-NMR spectra were recorded on JEOL NMR spectrometers (400 MHz for proton and 100 MHz for carbon) at ambient temperature. All chemical shifts (δ) are reported in part per million (ppm) down field from TMS; *J* values are given in Hz. The abbreviations used for NMR signals are: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet.

IR spectra were recorded on a SHIMADZU FTIR-8400S instrument (KBr pellet).

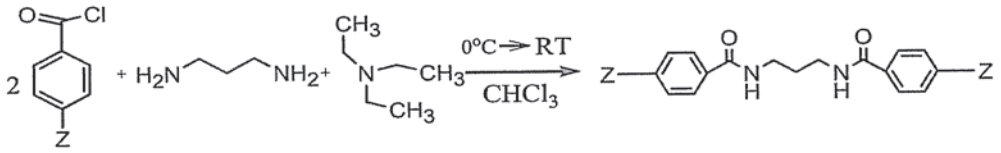
Melting points were determined on a MELTEMP apparatus and uncorrected.

The microscope images were obtained on a NIKON ECLIPSE E200 microscope.

## 3.1 THE SYNTHESIS OF N,N'-(PROPANE-1,3-DIYL)BIS(4-*p*-ARYLBENZAMIDE) ($B_1$-$B_{10}$)

### 3.1.1 The General Procedure

Bis *p*-aryl amides were synthesized by the reaction of *para*-substituted benzoyl chlorides and 1,3-diaminopropane in the presence of triethylamine in chloroform at 0°C (Scheme 3.1). Benzoyl chloride was added dropwise to a stirred chloroform solution of 1,3-diaminopropane at 0°C. The reaction mixture was allowed to stand at room temperature for 5 hours. After completion of the reaction, the chloroform mixture was washed with brine, chloroform layer was separated. After removal of chloroforom by rotary evaporation, the solid residue was purified by recrystallization from absolute ethanol. Subsequent filtration followed by drying under vacuum afforded bis-(*p*-aryl) amides as white solids.



Z: methyl ($B_1$), ethyl ($B_2$), propyl ($B_3$), butyl ($B_4$), hexyl ($B_6$), heptyl ($B_7$), decyl ($B_{10}$).

**Scheme 3.1.** General synthesis for bis amide derivatives

### 3.1.1.1 N,N'-(PROPANE-1,3-DIYL)BIS(4-METHYLBENZAMIDE), $B_1$

According to the general procedure, N,N'-(propane-1,3-diyl)bis(4-methylbenzamide), $B_1$ was prepared by using 5.2 g (33.73 mmol) of 4-methylbenzoyl chloride, 1 g (13.49 mmol) of 1,3-diaminopropane and 8.19 g (80.94 mmol) of triethyl amine in 25 ml of chloroform.

White solid, yield: 4.88 g (85%), melting point: 175.2-175.9°C

IR (KBr, $cm^{-1}$); 3333 (N-H stretching), 3063, 3028 (Ar-H), 2939 (Aliphatic C-H), 1639 (Amide Carbonyl), 1550,1508 (N-H bending) (Figure 3.1)

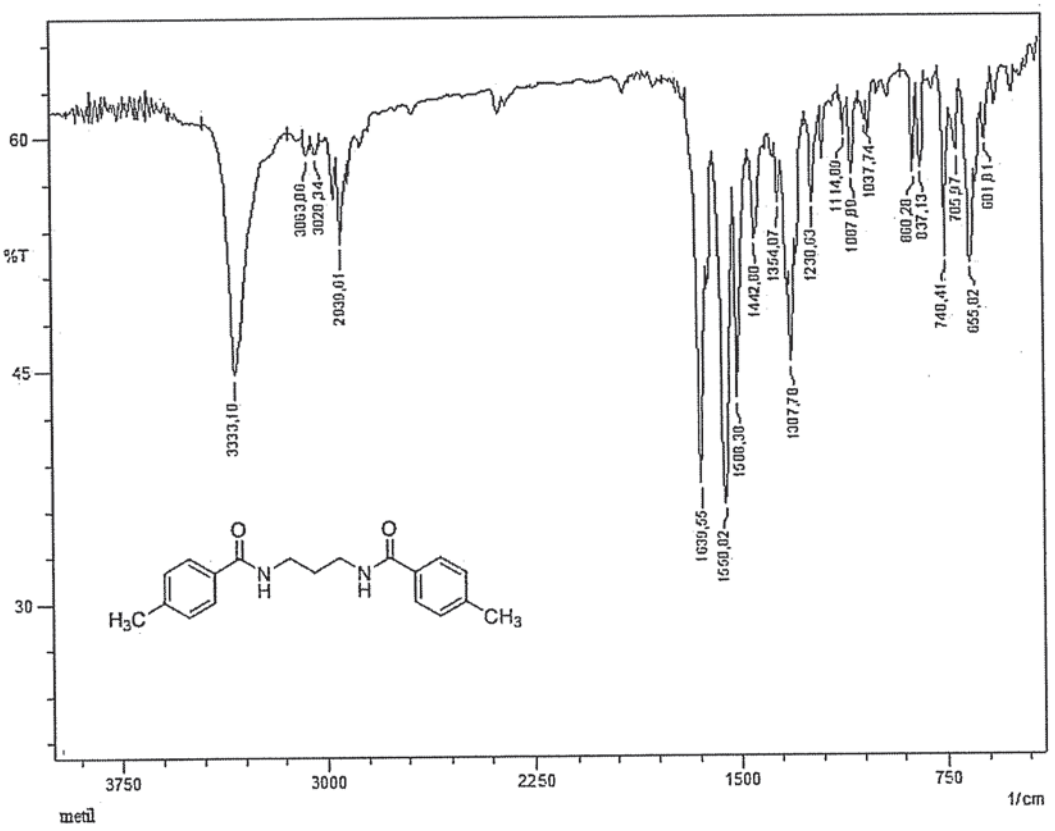



**Figure 3.1.** IR Spectrum of compound $B_1$

$^1$H NMR (400 MHz, $CDCl_3$) δ, ppm: 7.76 (d, $J$ = 8.0 Hz, 4H, Ar-H), 7.33 (t, $J$ = 8.0 Hz, 2H, NH), 7.21 (d, $J$ = 8.0 Hz, 4H, Ar-H), 3.50 (q, $J$ = 8.0 Hz, 4H, -$CH_2$), 2.37 (s, 6H, -$CH_3$), 1.73 – 1.79 (m, 2H, -$CH_2$) (Figure 3.2)

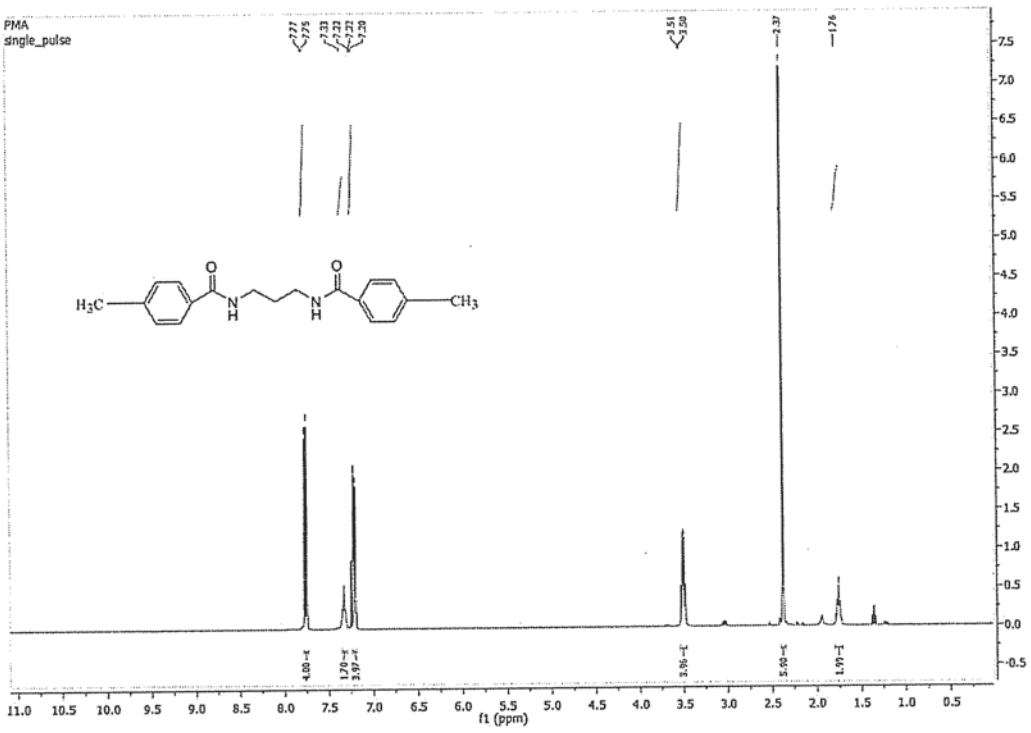



**Figure 3.2.** 400 MHz $^{1}$H NMR spectrum of compound $B_1$ in $CDCl_3$

$^{13}$C NMR (100 MHz, $CDCl_3$ ) δ, ppm: 168.28, 141.98, 131.48, 129.31, 127.12, 36.17, 29.97, 21.54 (Figure 3.3)

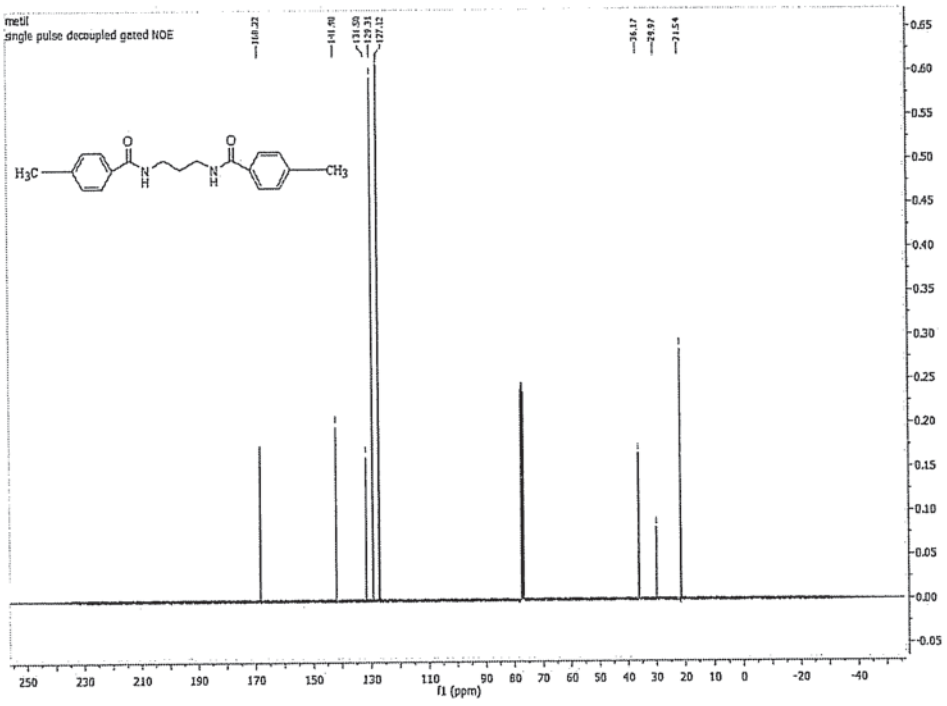



**Figure 3.3.** 100 MHz $^{13}C$ NMR spectrum of compound $B_1$ in $CDCl_3$

### 3.1.1.2 N,N'-(PROPANE-1,3-DIYL)BIS(4-ETHYLBENZAMIDE), $B_2$

According to the general procedure, N,N'-(propane-1,3-diyl)bis(4-ethylbenzamide), $B_2$ was prepared by using 3 g (17.79 mmol) of 4-ethylbenzoyl chloride and 0.527 g (7.12 mmol) of 1,3-diaminopropane and 4.32 g (42.72 mmol) of triethyl amine in 25 ml of chloroform.

White solid, yield: 1.76 g (88%), melting point: 147.0-147.6°C

IR (KBr, $cm^{-1}$); 3348 (N-H), 3033,3032 (Ar-H), 2962, 2935, 2874 (Aliphatic C-H), 1627 (Amide Carbonyl), 1548, 1504 (N-H bending) (Figure 3.4)

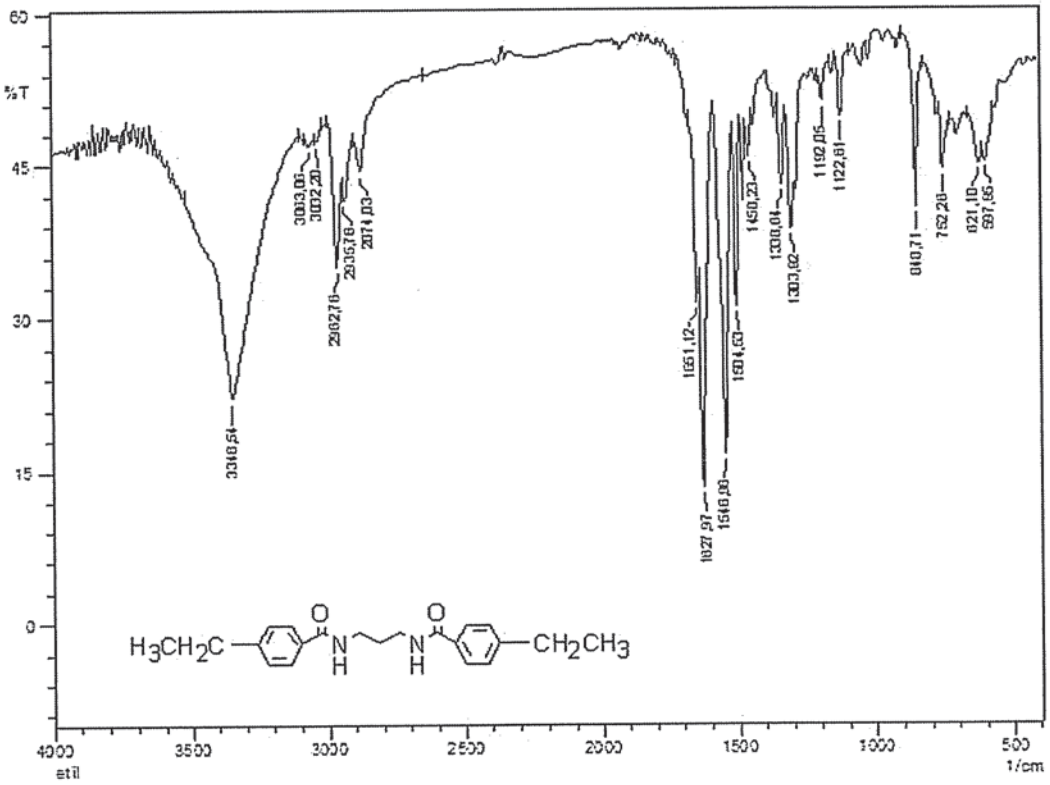



**Figure 3.4.** IR Spectrum of compound $B_2$

$^1$H NMR (400 MHz, $CDCl_3$ ) δ, ppm: 7.77 (d, $J$ = 8.0 Hz, 4H, Ar- H), 7.25 (t, $J$ = 8.0 Hz, 2H, -NH), 7.21 (d, $J$ = 8.0 Hz, 4H, -Ar-H), 3.51 (q, $J$ = 8.0 Hz, 4H, -$CH_2$), 2.67 (q, $J$ = 7.6 Hz, 4H, -$CH_2$), 1.74-1,80 (m, 2H, -$CH_2$), 1.22 (t, $J$ = 7.6 Hz, 6H, -$CH_3$). (Figure 3.5)

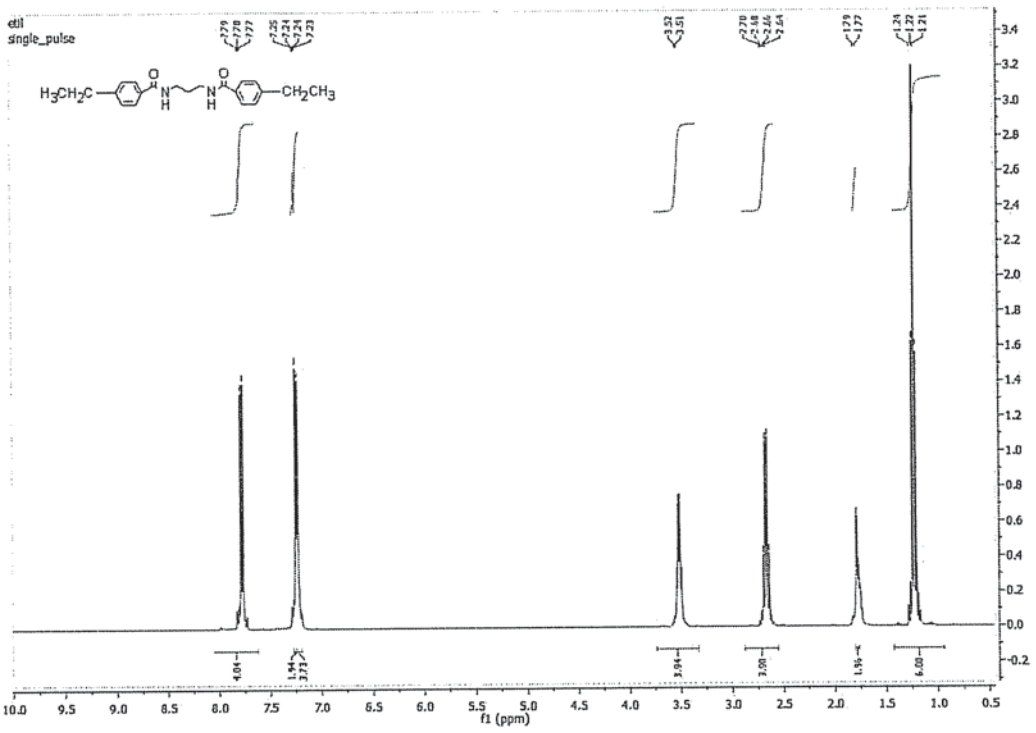



**Figure 3.5.** 400 MHz $^{1}H$ NMR spectrum of compound $B_2$ in $CDCl_3$

$^{13}C$ NMR (100 MHz, $CDCl_3$ ) δ, ppm: 168.8, 148.3, 131.8, 128.2, 127.2, 36.1, 30.1, 28.9, 15.4. (Figure 3.6)

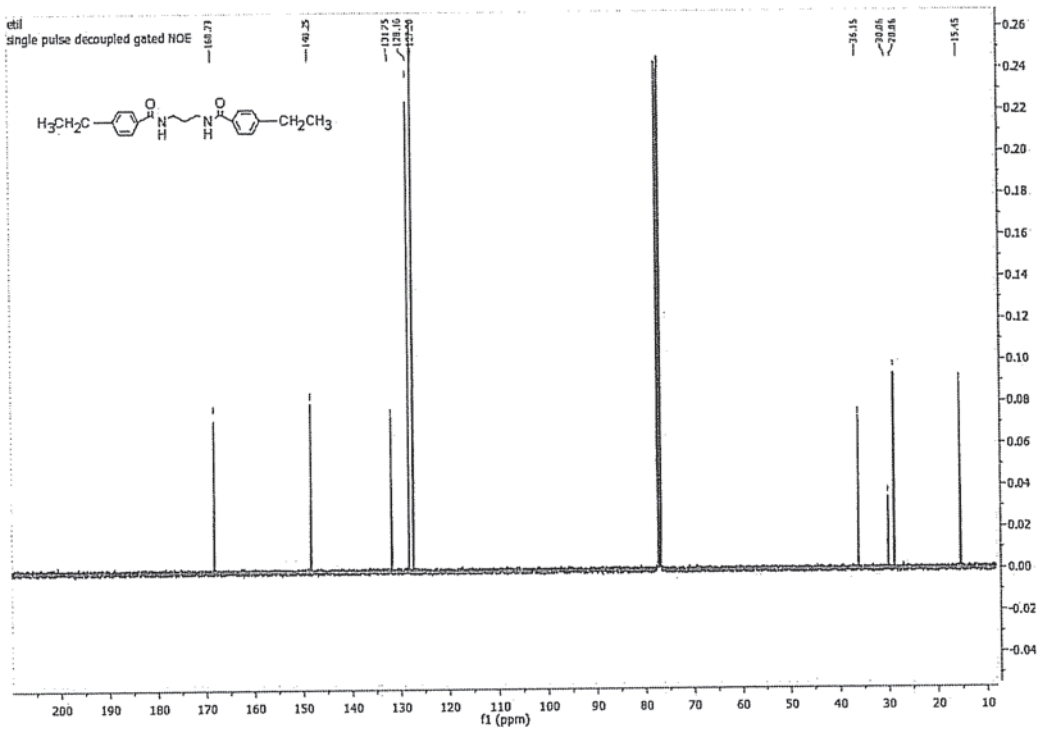



**Figure 3.6.** 100 MHz $^{13}C$ NMR spectrum of compound $B_2$ in $CDCl_3$

### 3.1.1.3 N,N'-(PROPANE-1,3-DIYL)BIS(4-PROPYLBENZAMIDE), $B_3$

According to the general procedure, N,N'-(propane-1,3-diyl)bis(4-propylbenzamide), $B_3$ was prepared by using 2 g (10.95 mmol) of 4-propylbenzoyl chloride and 0.325 g (4.38 mmol) of 1,3-diaminopropane and 2.66 g (26.28 mmol) of triethyl amine in 25 ml of chloroform.

White solid yield: 1.83 g (91%), melting point: 142.3-143.2°C

IR (KBr, $cm^{-1}$); 3319 (N-H stretching), 3080,3045 (Ar-H), 2963,2929,2870 (Aliphatic C-H), 1629 (Amide Carbonyl), 1545,1508 (N-H bending) (Figure 3.7)

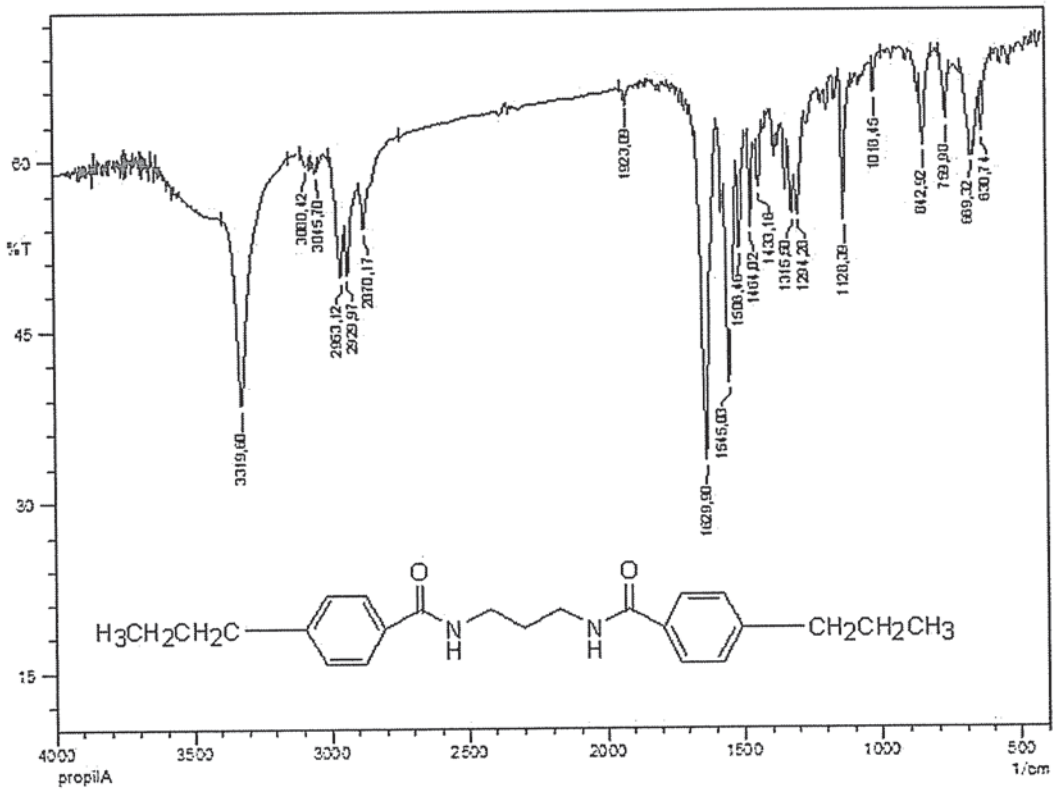



**Figure 3.7.** IR Spectrum of compound $B_3$

$^1$H NMR (400 MHz, $CDCl_3$ ): δ, ppm: 7.77 (d, $J$ = 8.0 Hz, 4H, Ar-H), 7.27 (t, $J$ = 4.0 Hz, 2H, NH), 7.21 (d, $J$ = 8.0 Hz, 4H, Ar-H), 3.51 (q, $J$ = 4.0 Hz, 4H, -$CH_2$), 2.60 (t, $J$ = 8.0 Hz, 4H, -$CH_2$), 1.73-1.79 (m, 2H, -$CH_2$), 1.58-1.67 (m, 4H, -$CH_2$), 0.91 (t, $J$ = 8.0 Hz, 6H, -$CH_3$) (Figure 3.8).

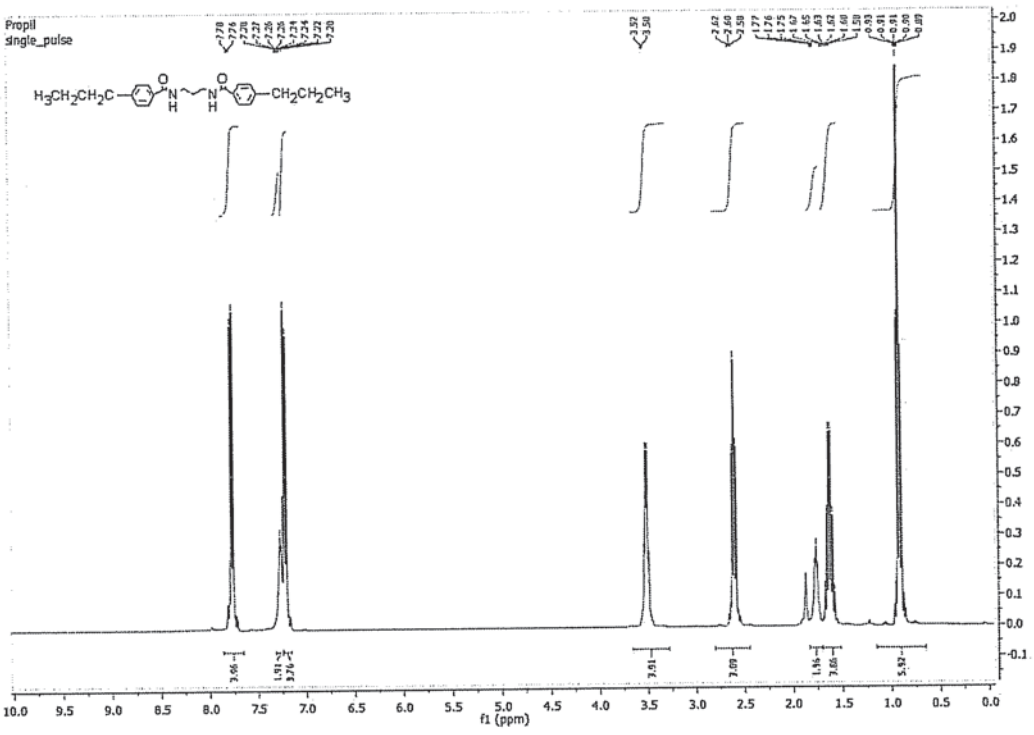



**Figure 3.8.** 400 MHz $^{1}H$ NMR spectrum of compound $B_3$ in $CDCl_3$

$^{13}C$ NMR (100 MHz, $CDCl_3$ ) δ, ppm: 168.2, 146.7, 131.8, 128.8, 127.1, 37.9, 36.1, 30.1, 24.4, 13.8 (Figure 3.9).

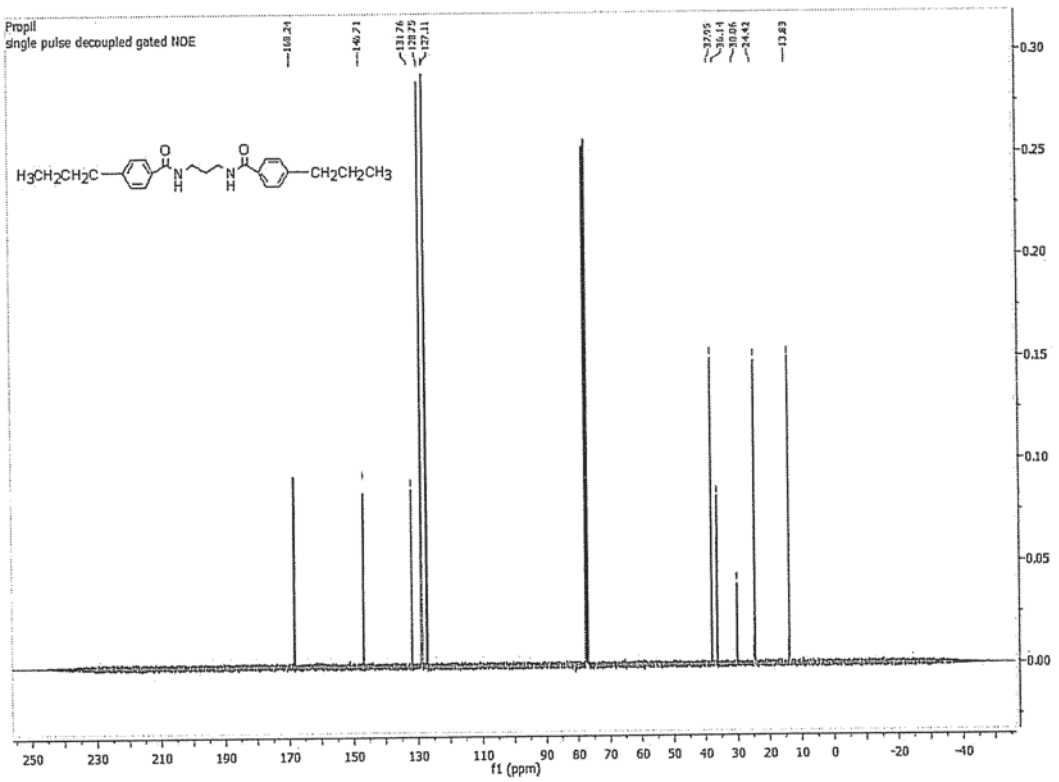



**Figure 3.9.** 100 MHz $^{13}C$ NMR spectrum of compound $B_3$ in $CDCl_3$

### 3.1.1.4 N,N'-(PROPANE-1,3-DIYL)BIS(4-BUTYLBENZAMIDE), $B_4$

According to the general procedure, N,N'-(propane-1,3-diyl)bis(4-butylbenzamide), $B_4$ was prepared by using 3 g (15.25 mmol) of 4-butylbenzoyl chloride and 0.452 g (6.10 mmol) of 1,3-diaminopropane and 3.70 g (36.6 mmol) of triethyl amine in 25 ml of chloroform.

White solid, yield: 1.67 g (83%), melting point: 132.5-133.8°C

IR (KBr, $cm^{-1}$); 3323 (N-H stretching), 3080,3045 (Ar-H), 2872,2854 (Aliphatic C-H), 1627 (Amide Carbonyl), 1545,1508 (N-H bending) (Figure 3.10)

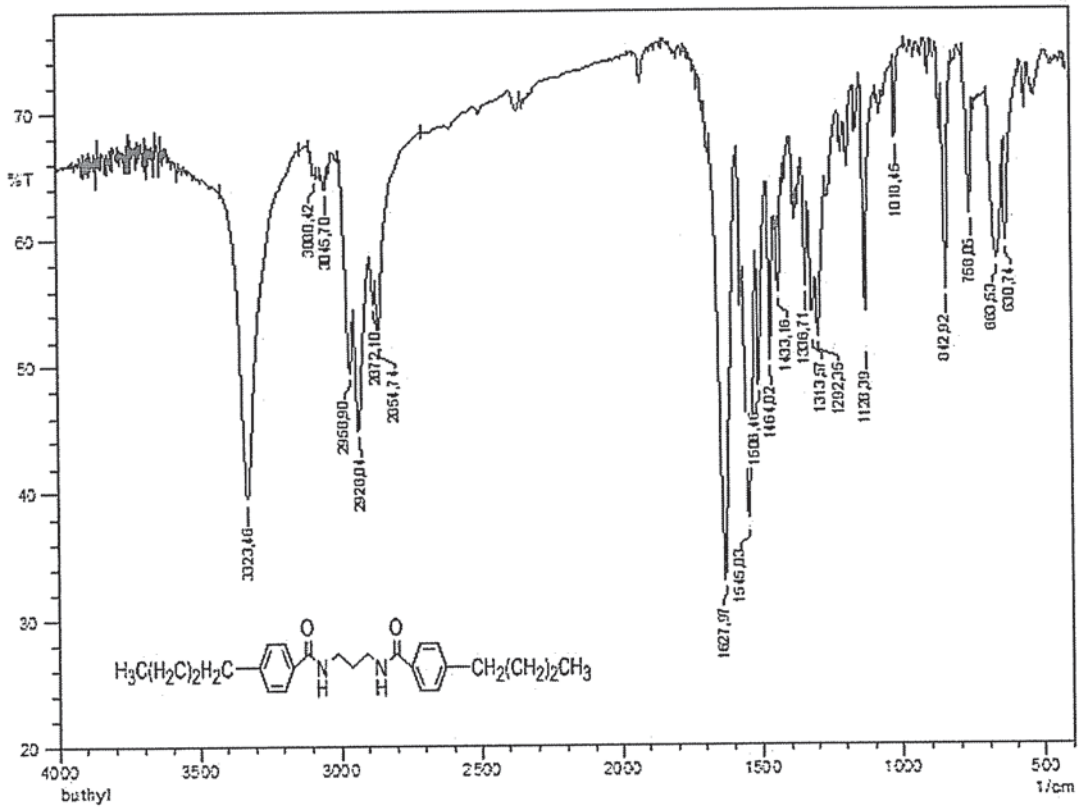



**Figure 3.10.** IR Spectrum of compound $B_4$

$^1$H NMR (400 MHz, $CDCl_3$ ): δ, ppm: 7.77 (d, $J$ = 8.0 Hz, 4H, Ar-H), 7.32 (t, $J$ = 4.0 Hz, 2H, NH), 7.21 (d, $J$ = 8.0 Hz, 4H, Ar-H), 3.51 (d, $J$ = 4.0 Hz, 4H, -$CH_2$), 2.62 (t, $J$ = 8.0 Hz, 4H), 1.73 – 1.79 (m, 2H, -$CH_2$), 1.54 – 1.61 (m, 4H, -$CH_2$), 1.28-1,37 (m, 4H. –$CH_2$), 0.90 (t, $J$ = 8.0 Hz, 6H, -$CH_3$) (Figure 3.11).

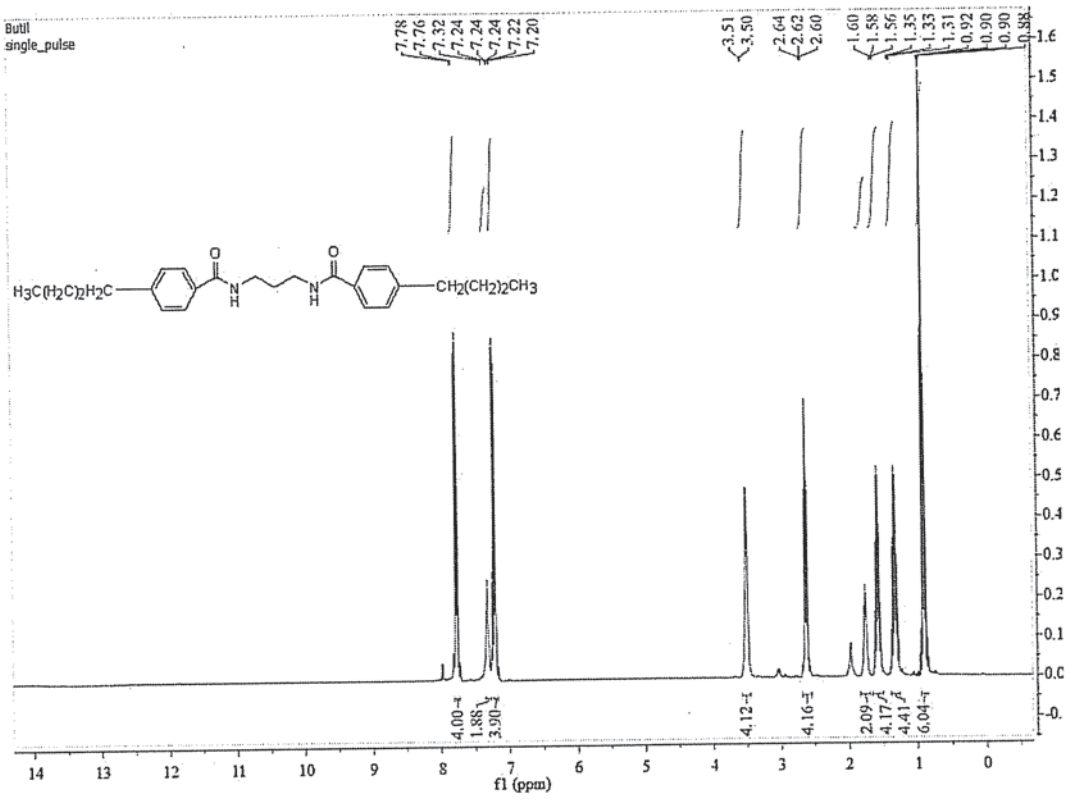



**Figure 3.11.** 400 MHz $^{1}$H NMR spectrum of compound $B_4$ in $CDCl_3$

$^{13}$C NMR (100 MHz, $CDCl_3$ ) δ, ppm: 168.2, 146.9, 131.7, 128.7, 127.1, 36.2, 35.6, 33.4, 30.0, 22.4, 14.0 (Figure 3.12).

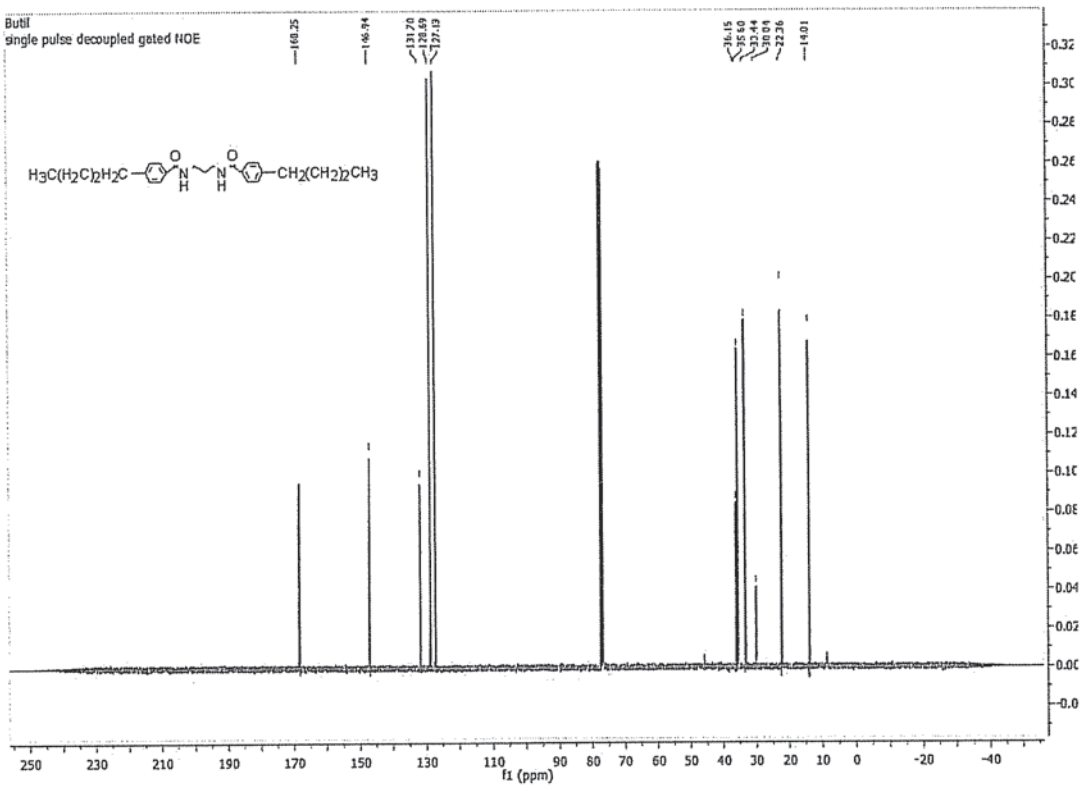



**Figure 3.12.** 100 MHz $^{13}C$ NMR spectrum of compound $B_4$ in $CDCl_3$

### 3.1.1.5 N,N'-(PROPANE-1,3-DIYL)BIS(4-HEXYLBENZAMIDE), $B_6$

According to the general procedure, N,N'-(propane-1,3-diyl)bis(4-hexylbenzamide), $B_6$ was prepared by using 2 g (8.899 mmol) of 4-hexylbenzoyl chloride and 0.264 g (3.560 mmol) of 1,3-diaminopropane and 2.16 g (21.358 mmol) of triethyl amine in 25 ml of chloroform.

White solid, yield: 1.70 g (85%), melting point: 138.2-139.5°C

IR (KBr, $cm^{-1}$); 3321 (N-H stretching), 3082,3047 (Ar-H), 2958, 2926,2854 (Aliphatic C-H), 1627 (Amide Carbonyl), 1543 (N-H bending) (Figure 3.13)

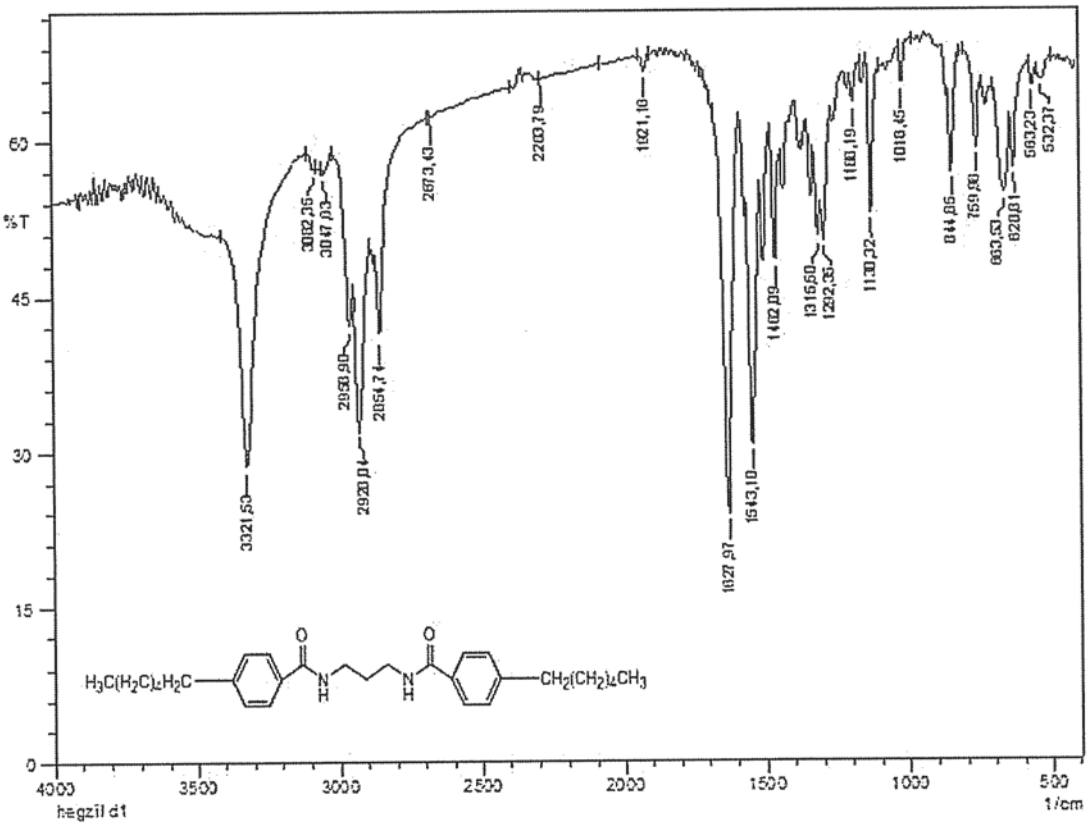



**Figure 3.13.** IR Spectrum of compound $B_6$

$^1$H NMR (400 MHz, $CDCl_3$ ): δ, ppm: 7.77 (d, $J$ = 8.0 Hz, 4H, Ar-H), 7.25 ( t, $J$ = 4.0 Hz, 2H, NH), 7.21 (d, $J$ = 8.0 Hz, 4H, Ar-H), 3.51 (q, $J$ = 4.0 Hz, 4H, -$CH_2$), 2.62 (t, $J$ = 8.0 Hz, 4H, -$CH_2$), 1.73-1,79 (m, 2H, -$CH_2$), 1.55 – 1.62 (m, 4H, -$CH_2$), 1.28 (br m, 12H, -$CH_2$), 0.86 (t, $J$ = 8.0 Hz, 6H, -$CH_3$) (Figure 3.14).

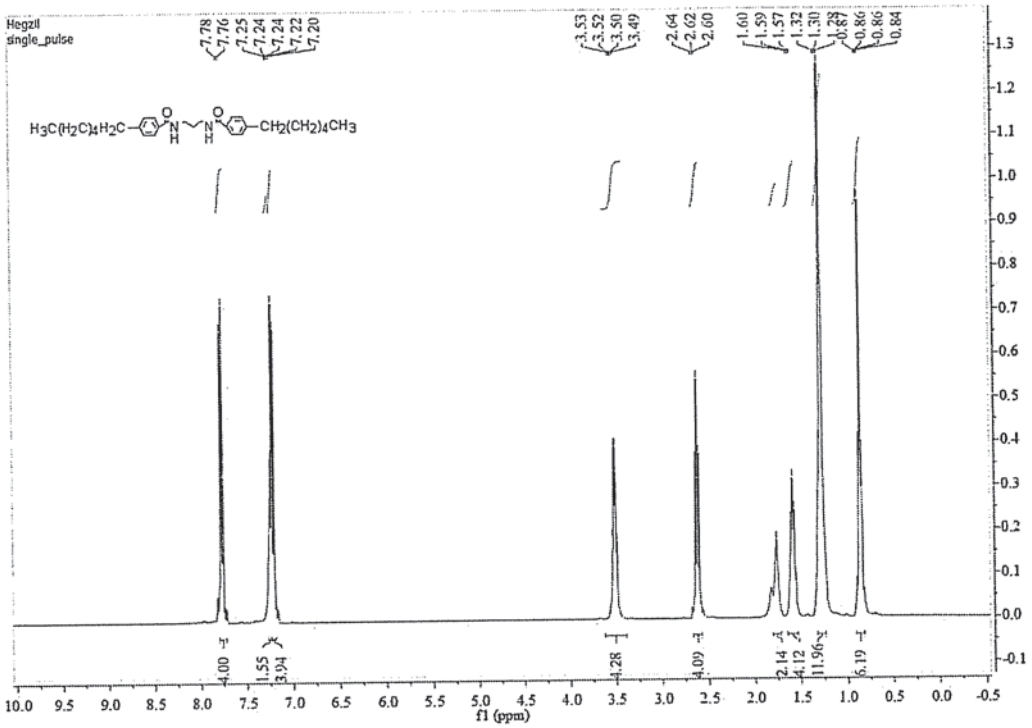



**Figure 3.14.** 400 MHz $^{1}$H NMR spectrum of compound $B_6$ in $CDCl_3$

$^{13}$C NMR (100 MHz, $CDCl_3$ ) δ, ppm: 168.3, 146.9, 131.8, 128.7, 127.1, 36.1, 35.9, 31.8, 31.3, 30.1, 29.0, 22.7, 14.2 (Figure 3.15).

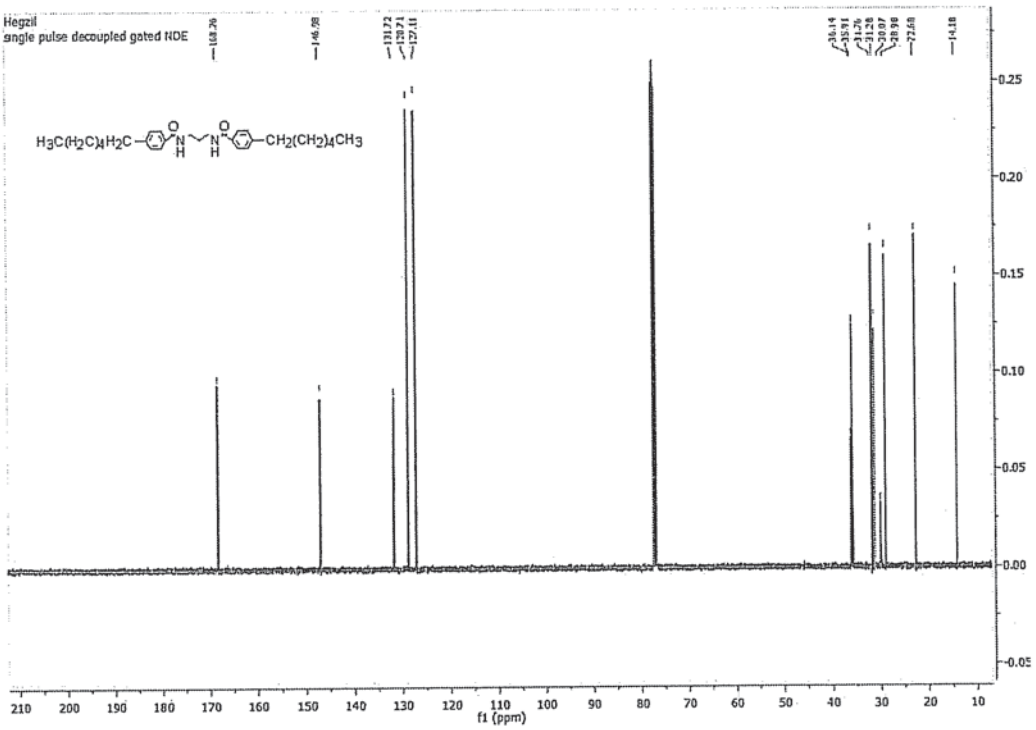



**Figure 3.15.** 100 MHz $^{13}C$ NMR spectrum of compound $B_6$ in $CDCl_3$

### 3.1.1.6 N,N'-(PROPANE-1,3-DIYL)BIS(4-HEPTYLBENZAMIDE), $B_7$

According to the general procedure, N,N'-(propane-1,3-diyl)bis(4-heptylbenzamide), $B_7$ was prepared by using 2 g (8.377 mmol) of 4-heptylbenzoyl chloride and 0.248 g (3.351 mmol) of 1,3-diaminopropane and 2.03 g (20.105 mmol) of triethyl amine in 25 ml of chloroform.

White solid, yield:1.80 g (90%), melting point: 136.8-138.0°C

IR (KBr, $cm^{-1}$); 3321 (N-H stretching), 3039 (Ar-H), 2955, 2924,2850 (Aliphatic C-H), 1627 (Amide Carbonyl), 1543 (N-H bending) (Figure 3.16)

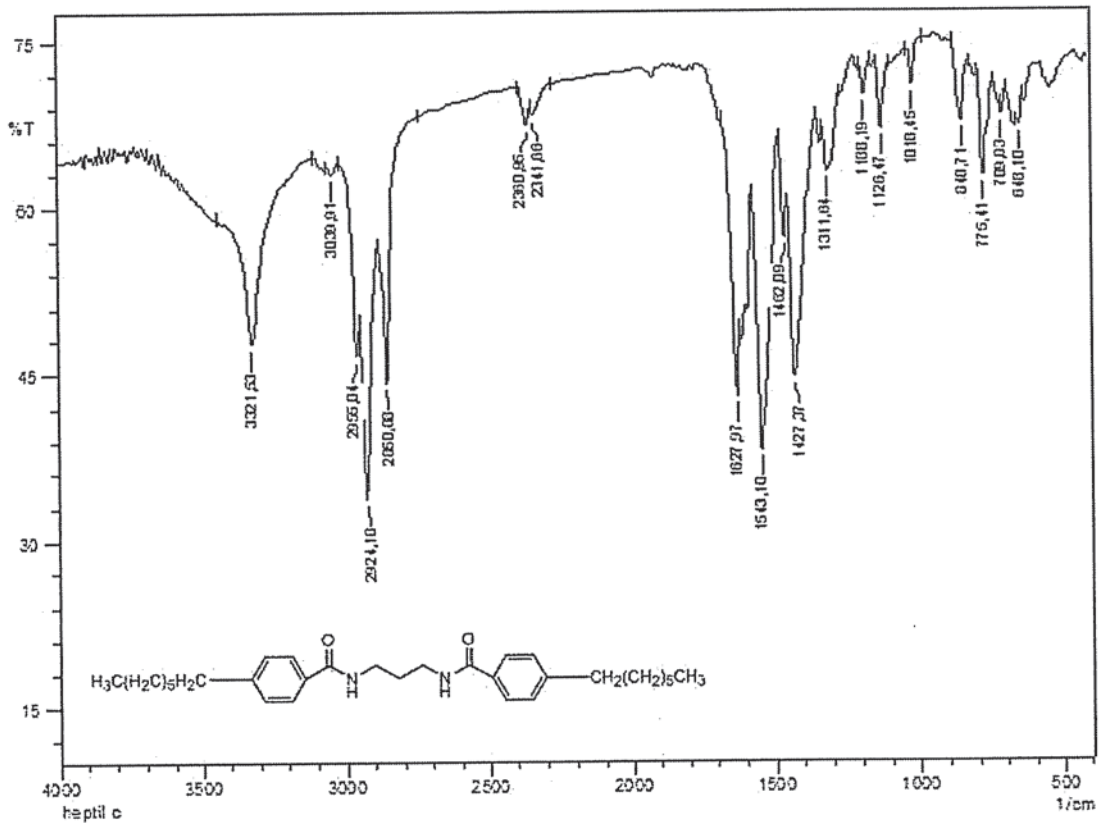



**Figure 3.16.** IR Spectrum of compound $B_7$

$^1$H NMR (400 MHz, $CDCl_3$ ): δ, ppm: 7.76 (d, $J$ = 8.0 Hz, 4H, Ar-H), 7.24 (s, 2H, -NH), 7.21 (d, $J$ =8.0 Hz, 4H, Ar-H), 3.50 (br q, 4H, -$CH_2$), 2.61 (t, $J$ = 8.0 Hz, 4H, -$CH_2$), 1.55-1,62 (br m, 2H, -$CH_2$), 1.23 – 1.31 (br m, 20H, -$CH_2$), 0.86 (t, $J$ = 8.0 Hz, 6H, -$CH_3$) (Figure 3.17).

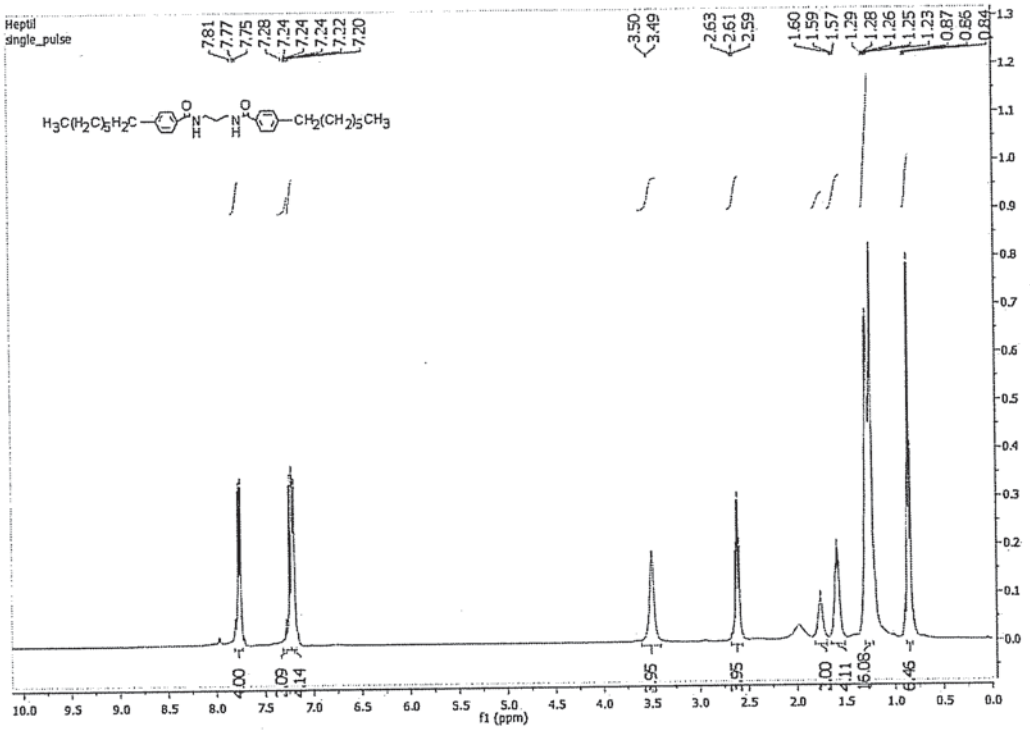



**Figure 3.17.** 400 MHz $^{1}$H NMR spectrum of compound $B_7$ in $CDCl_3$

$^{13}$C NMR (100 MHz, $CDCl_3$ ) δ, ppm: 168.2, 147.0, 131.7, 128.7, 127.1, 36.2, 35.9, 31.9, 31.3, 29.8, 29.3, 29.2, 22.8, 22.7, 14.2 (Figure 3. 18).

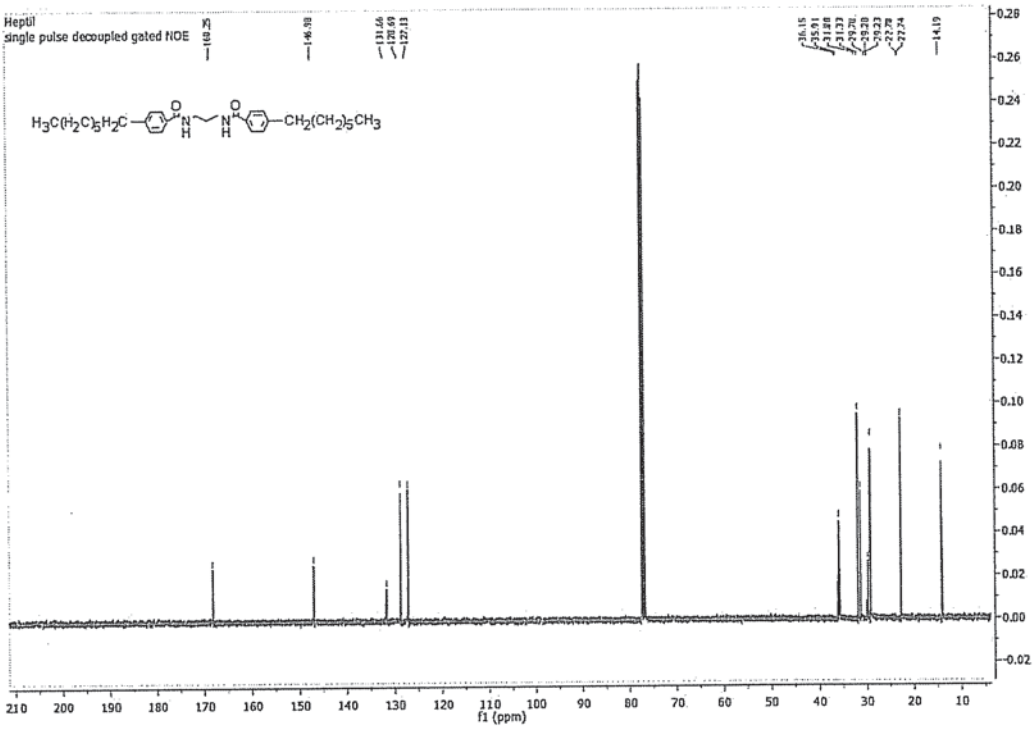



**Figure 3.18.** 100 MHz $^{13}C$ NMR spectrum of compound $B_7$ in $CDCl_3$

### 3.1.1.7 N,N'-(PROPANE-1,3-DIYL)BIS(4-DECYLBENZAMIDE), $B_{10}$

According to the general procedure, N,N'-(propane-1,3-diyl)bis(4-decylbenzamide), $B_{10}$ was prepared by using 3 g (10.68 mmol) of 4-decylbenzoyl chloride and 0.316 g (4.27 mmol) of 1,3-diaminopropane and 2.59 g (25.64 mmol) of triethyl amine in 25 ml of chloroform.

White solid, yield: 2.73. g (91%), melting point: 131.9-132.4°C

IR (KBr, $cm^{-1}$); 3340 (N-H stretching), 3082, 3051 (Ar-H), 2955, 2954, 2850 (Aliphatic C-H), 1627 (Amide Carbonyl), 1539, 1504 (N-H bending) (Figure 3.19)

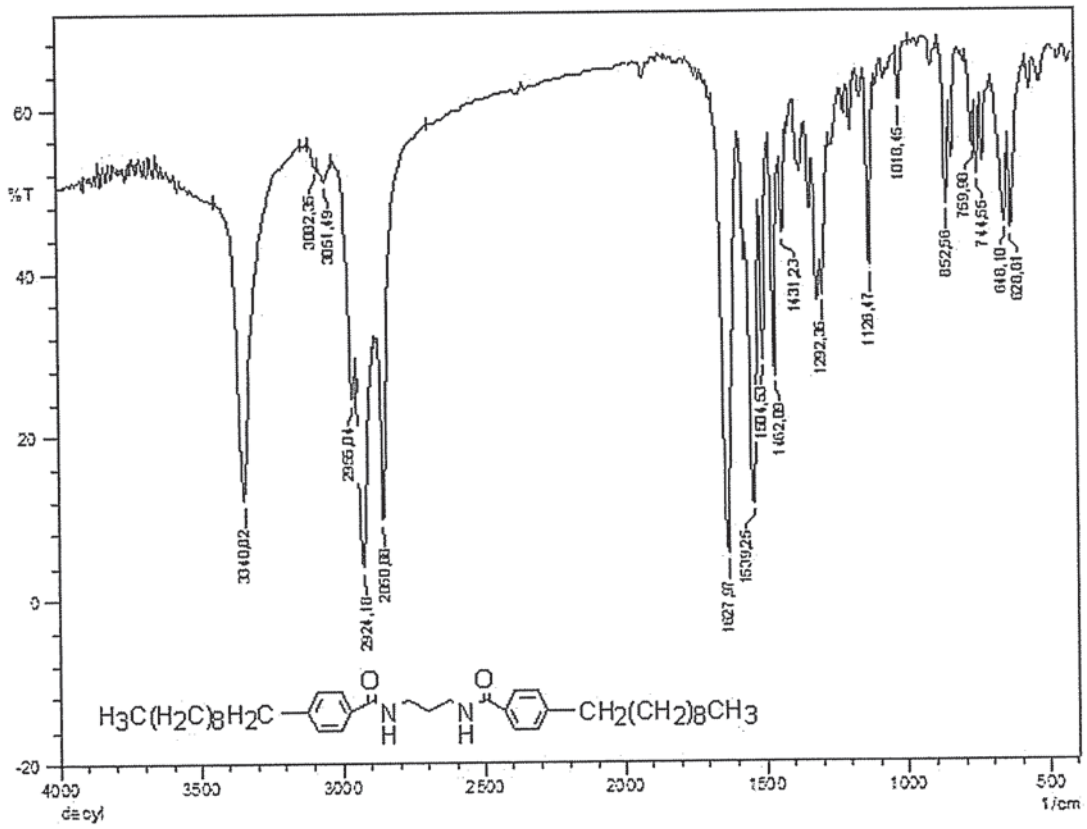



**Figure 3.19.** IR Spectrum of compound $B_{10}$

$^1$H NMR (400 MHz, $CDCl_3$ ): δ, ppm: 7.77 (t, $J$ = 8.0 Hz, 4H, Ar-H), 7.24 (s, 2H, -NH), 7.22 (d, $J$ = 8.0 Hz, 4H, Ar-H), 3.51 (q, $J$ = 4 Hz, 4H, -$CH_2$), 2.62 (t, $J$ = 8.0 Hz, 4H, -$CH_2$), 1.55 – 1.63 (m, 2H, -$CH_2$), 1.20 – 1.27 (m, 32H, -$CH_2$), 0.86 (t, $J$ = 8.0 Hz, 6H, -$CH_3$) (Figure 3.20).

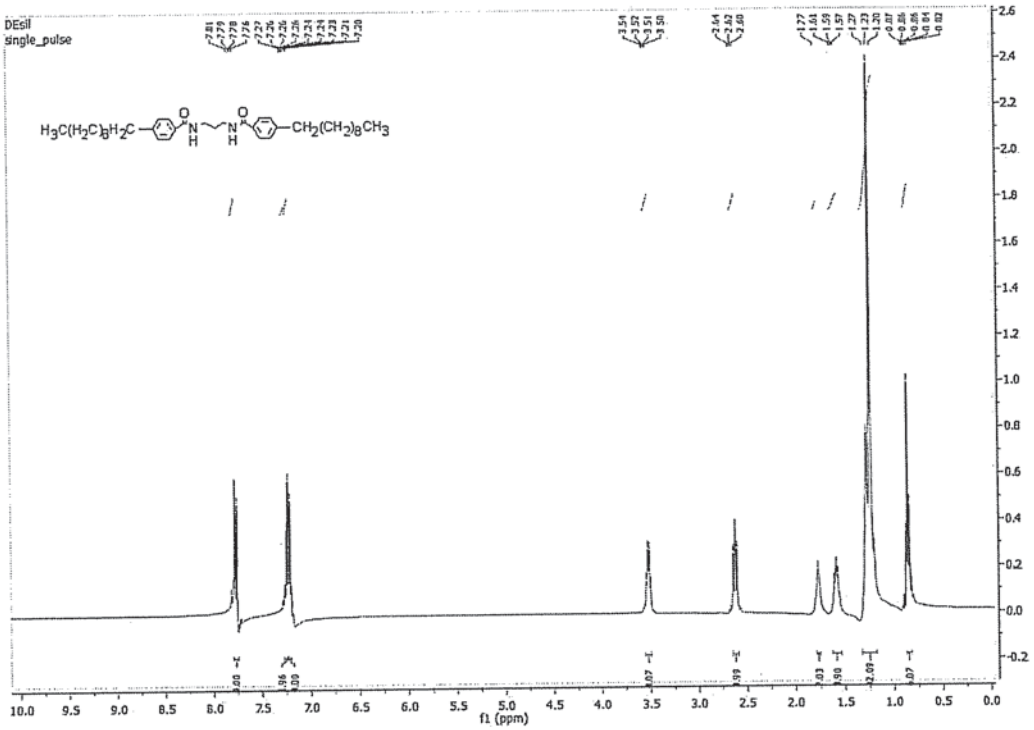



**Figure 3.20.** 400 MHz $^{1}$H NMR spectrum of compound $B_{10}$ in $CDCl_3$

$^{13}$C NMR (100 MHz, $CDCl_3$ ) δ, ppm: 168.2, 147.0, 131.7, 128.7, 127.1, 36.1, 35.9, 31.98, 31.3, 30.1, 29.7, 29.7, 29.6, 29.4, 29.3, 22.8, 14.2 (Figure 3.21).

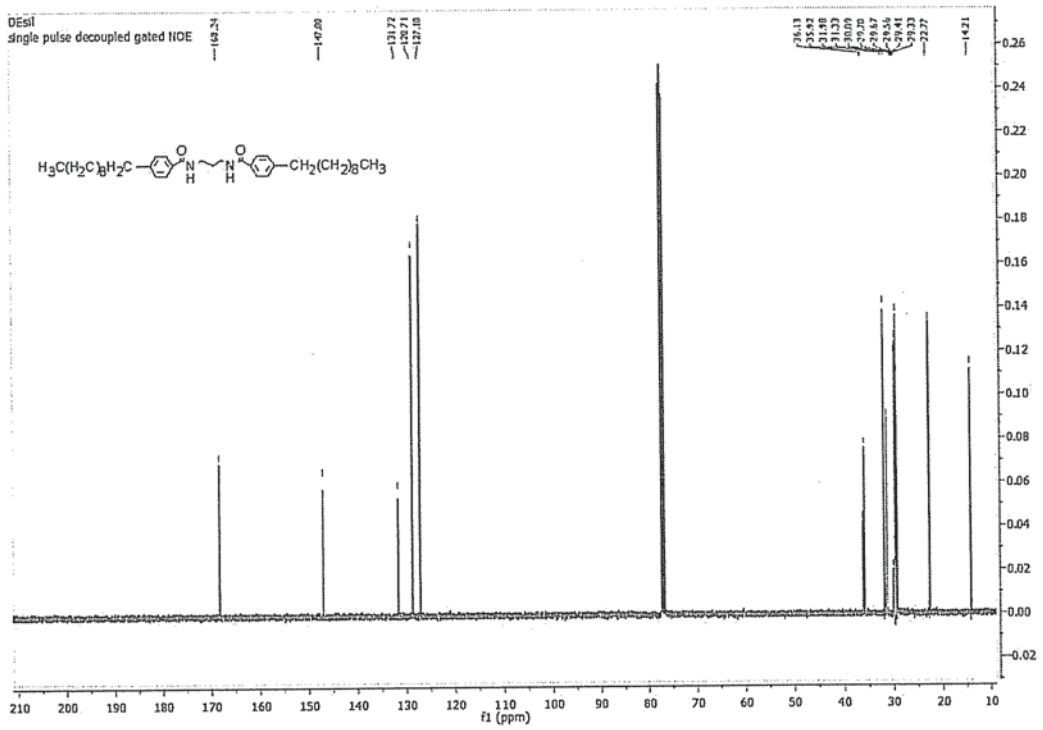



**Figure 3.21.** 100 MHz $^{13}C$ NMR spectrum of compound $B_{10}$ in $CDCl_3$

## 3.2 Gel Preparation

Gel preparation involves several steps:

1. A weighted amount of gelator and a measured volume of organic solvent were added into a vial (diameter: 15 mm).
2. The system was heated over the hot plate until the solid was completely dissolved.
3. Then the hot solution was cooled to room temperature and kept for 24 hours for stability.
4. Opaque and white gel was occured and the gelation was tested by test tube inversion method.

## 3.3 Test Tube Inversion (Inverse Flow) Method and Determination of Minimum Gelation Concentration (mgc)

The minimum concentration required for a homogeneous gel sample without gravitational flow is known as minimum gelation concentration (mgc). For this purpose, mixtures of each compound was prepared in organic solvents and heated to get a homogenous solution. Then the resulting solution was allowed to cool to room temperature or -18 °C. It is considered that gelation was complete when a homogeneous sample without any gravitational flow was obtained (Demir-Ordu, et al. 2015).

# 4 RESULT AND DISCUSSIONS

## 4.1 The Synthesis of N,N'-(Propane-1,3-Diyl)Bis-(4-*p*-Arylbenzamide) ($B_1$-$B_{10}$)

The main purpose of the present work was to obtain new bis amide derivatives and to study their gelation properties in various organic solvents.

Bis-(*p*-aryl) amides ($B_1$-$B_{10}$) were synthesized by the reaction of 1,3-diaminopropane with suitable benzoyl chlorides in 83-91% yields (Table 4.1).

**Table 4.1.** The yields of the synthesized Bis-(*p*-aryl) ($B_1$- $B_{10}$)

| Compound | Z | Yield ( g / % ) | | Melting point (°C) |
|---|---|---|---|---|
| $B_1$ | Methyl | 4.88 | 85 | 175.2-175.9 |
| $B_2$ | Ethyl | 1.76 | 88 | 147.0-147.6 |
| $B_3$ | Propyl | 1.83 | 91 | 142.3-143.2 |
| $B_4$ | Butyl | 1.67 | 83 | 132.5-133.8 |
| $B_6$ | Hexyl | 1.70 | 85 | 138.2-139.5 |
| $B_7$ | Heptyl | 1.83 | 90 | 136.8-138.0 |
| $B_{10}$ | Decyl | 2.73 | 91 | 131.9-132.4 |

## 4.2 Structure Elucidation of $B_1$-$B_{10}$ Derivatives by IR and NMR Spectroscopy

The structures of the compounds ($B_1$-$B_{10}$) were determined by IR, $^1$H NMR and $^{13}$C NMR analyses. IR spectra of $B_1$-$B_{10}$ exhibited common characteristic absorption bands at 3319-3333 $cm^{-1}$ (NH) and 1639-1627 $cm^{-1}$ (Amide Carbonyl) for amide funcitonality. The IR spectrum of compound $B_1$ was given as an example in Figure 4.1 The IR data for all compounds was tabulated in Table 4.2.

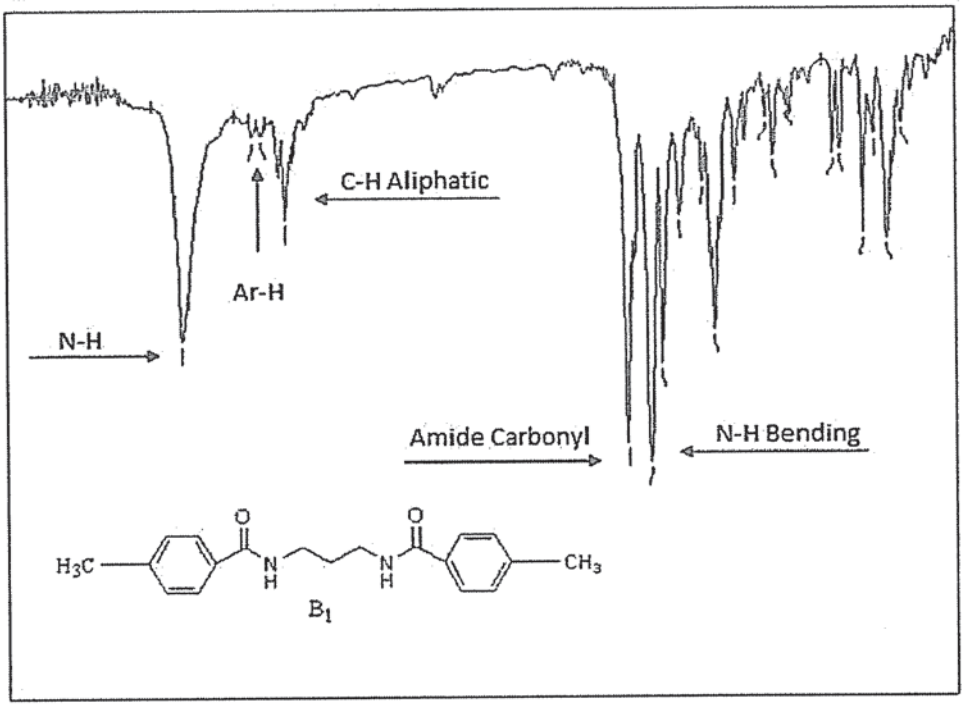



**Figure 4.1.** IR spectrum of compound $B_1$

**Table 4.2.** IR data for the compounds $B_1$- $B_{10}$

| | IR ($\nu_{max/cm}^{-1}$) | | | | |
|---|---|---|---|---|---|
| COMPOUND | N-H Stretching | Ar-H | C-H Stretching | Amide Carbonyl | N-H Bending |
| $B_1$ | 3333 | 3063,3028 | 2939 | 1639 | 1550,1508 |
| $B_2$ | 3348 | 3033,3032 | 2935 | 1627 | 1548,1504 |
| $B_3$ | 3319 | 3080,3045 | 2929 | 1629 | 1545,1508 |
| $B_4$ | 3323 | 3080,3045 | 2872 | 1627 | 1545,1508 |
| $B_6$ | 3321 | 3082,3047 | 2926 | 1627 | 1543 |
| $B_7$ | 3321 | 3039 | 2924 | 1627 | 1543 |
| $B_{10}$ | 3340 | 3082,3051 | 2850 | 1627 | 1539,1504 |

The purpose of the work was also to find the effect of the length of *p*-alkyl substitutiens on the gelation ability. Therefore, all compounds had *p*-substituted aromatic ring, a spacer with three methylene unit and amide functionality in common (Table 4.3) (Figure 4.2). For all compounds, the NH proton signals of the amide unit were observed at 7.24-7.33 ppm as triplets due to the coupling with the methylene protons ($H_c$). Aromatic protons $H_a$ were seen at 7.76-7.77 ppm as doublets that were more deshielded than the signals of $H_b$ protons (7.21-7.22 ppm) due to the electron

withdrawing characteristic of the amide carbonyl. The $H_c$ protons appeared as a quartet around 3.51 ppm as a result of the coupling between methylene ($H_d$) and NH protons. The $H_b$ protons observed as a multiplet between 1.73-1.79 ppm, respectively.

For compound $B_1$ (*p*-methyl), *p*-$CH_3$ hydrogens were observed as a singlet at 2.37 ppm. The *p*-$CH_2$ hydrogens of $B_3$ (*p*-propyl), $B_4$ (*p*-butyl), $B_6$ (*p*-heptyl), $B_7$ (*p*-hexyl), and $B_{10}$ were observed as triplets at around 2.60 ppm due to the coupling with the neighboring methylene protons. However, *p*-$CH_2$ protons of $B_2$ (*p*-ethyl) were seen as a quartet at 2.67 ppm due to the coupling with the neighboring methyl protons.

The chemical shifts of the other protons in the *p*-alkyl group were given in (Tables 4.4-4.10).

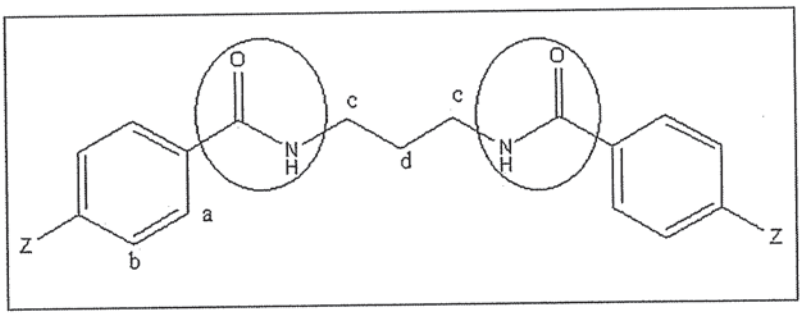



**Table 4.3.** 400 MHz $^1$H NMR data for compound $B_1$-$B_{10}$ in $CDCl_3$

| | δ (ppm) | | | | |
|---|---|---|---|---|---|
| Compound ID | NH | $H_a$ | $H_b$ | $H_c$ | $H_d$ |
| $B_1$ | 7.33 | 7.76 | 7.21 | 3.50 | 1.73-1.79 |
| $B_2$ | 7.25 | 7.77 | 7.21 | 3.51 | 1.74-1.80 |
| $B_3$ | 7.27 | 7.77 | 7.21 | 3.51 | 1.73-1.79 |
| $B_4$ | 7.32 | 7.77 | 7.21 | 3.51 | 1.73-1.79 |
| $B_6$ | 7.25 | 7.77 | 7.21 | 3.51 | 1.73-1.79 |
| $B_7$ | 7.24 | 7.76 | 7.21 | 3.50 | 1.55-1.62 |
| $B_{10}$ | 7.24 | 7.77 | 7.22 | 3.51 | 1.55-1.63 |

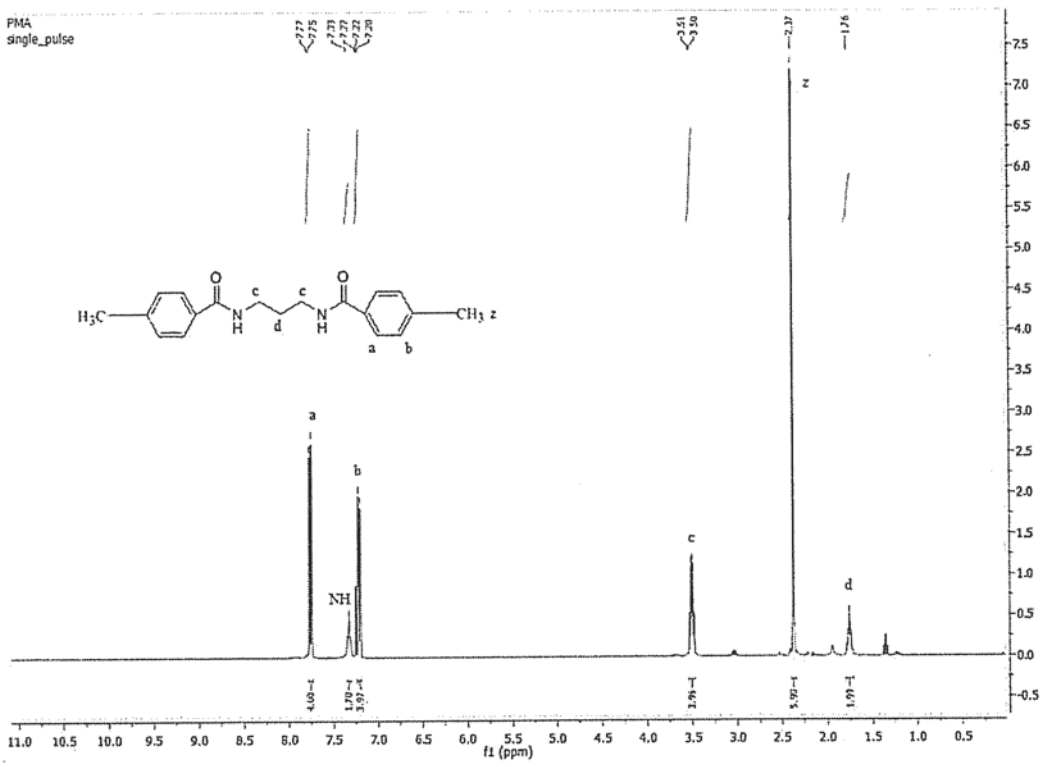
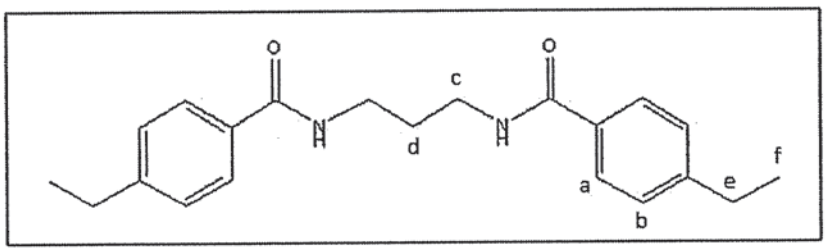


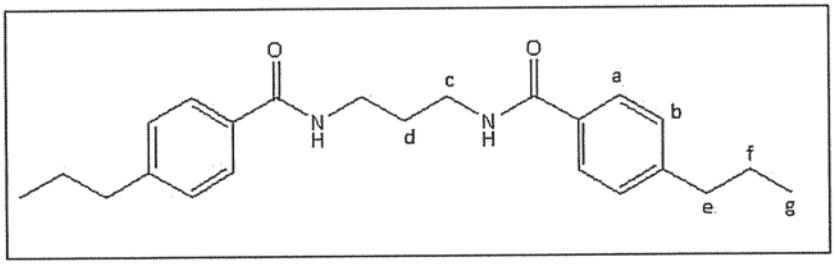

**Figure 4.2.** Principle proton NMR signals of $B_1$

**Table 4.4.** 400 MHz $^1H$ NMR data of $B_2$ in $CDCl_3$



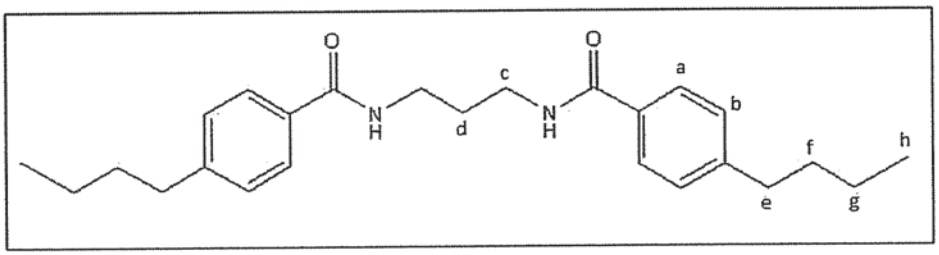
| | δ (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| COMP. | NH | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $H_f$ |
| $B_2$ | 7.25 | 7.77 | 7.21 | 3.51 | 1.74-1.80 | 2.67 | 1.22 |

**Table 4.5.** 400 MHz $^1$H NMR data of $B_3$ in $CDCl_3$



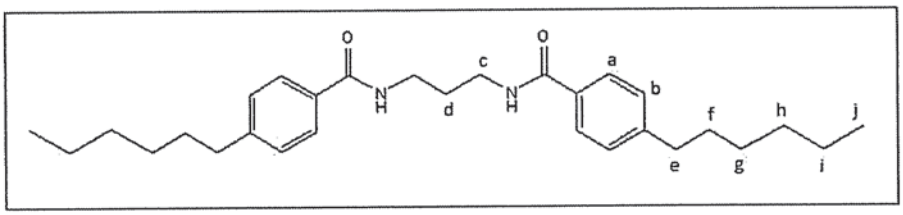

| | δ (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| COMP. | NH | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $H_f$ | $H_g$ |
| $B_3$ | 7.27 | 7.77 | 7.21 | 3.51 | 1.73-1.79 | 2.60 | 1.58-1.67 | 0.91 |

**Table 4.6.** 400 MHz $^1$H NMR data of $B_4$ in $CDCl_3$



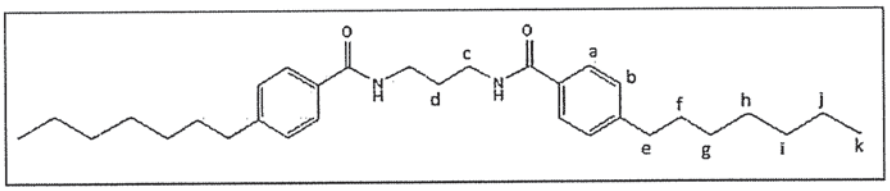

| | δ (ppm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| COMP | NH | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $H_f$ | $H_g$ | $H_h$ |
| $B_4$ | 7.32 | 7.77 | 7.21 | 3.51 | 1.73-1.79 | 2.62 | 1.54-1.61 | 1.28-1.37 | 0.90 |

**Table 4.7.** 400 MHz $^1$H NMR data of $B_6$ in $CDCl_3$



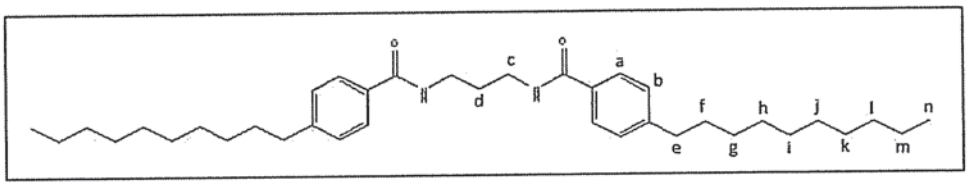

| | δ (ppm) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| COMP | NH | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $H_f$ | $H_{g\text{-}h\text{-}i}$ | $H_j$ |
| $B_6$ | 7.25 | 7.77 | 7.21 | 3.51 | 1.73-1.79 | 2.62 | 1.55-1.62 | 1.28 | 0.86 |

**Table 4.8.** 400 MHz $^1$H NMR data of $B_7$ in $CDCl_3$




| | δ (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| COMP. | NH | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $H_{f\text{-}g\text{-}h\text{-}i\text{-}j}$ | $H_k$ |
| $B_7$ | 7.24 | 7.76 | 7.21 | 3.50 | 1.55-1.62 | 2.61 | 1.23-1.31 | 0.86 |

**Table 4.9.** 400 MHz $^{1}H$ NMR data of $B_{10}$ in $CDCl_3$




| | δ (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| COMP. | NH | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $H_{f\text{-}g\text{-}h\text{-}i\text{-}j\text{-}k\text{-}l\text{-}m}$ | $H_n$ |
| $B_{10}$ | 7.24 | 7.77 | 7.22 | 3.51 | 1.55-1.63 | 2.62 | 1.20-1.27 | 0.86 |

The amide linkage in the structures of $B_1$-$B_{10}$ could also be proven by $^{13}C$ NMR spectrum. In the $^{13}C$ NMR spectra, the chemical shifts of the carbonyl carbons ($C_5$) were found to be at 168.2 ppm. Since carbon chain spacer between two amide units are common for all compounds, similar chemical shift values were obtained as indicated in Table 4.10 and Figure 4.3.

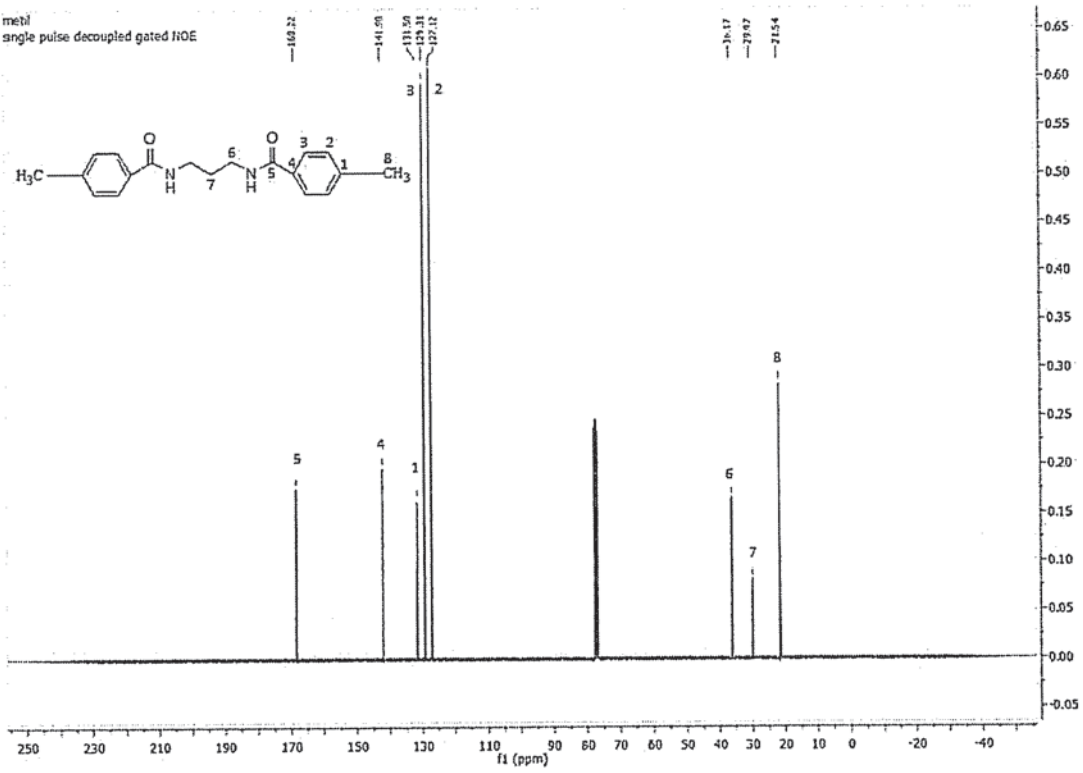
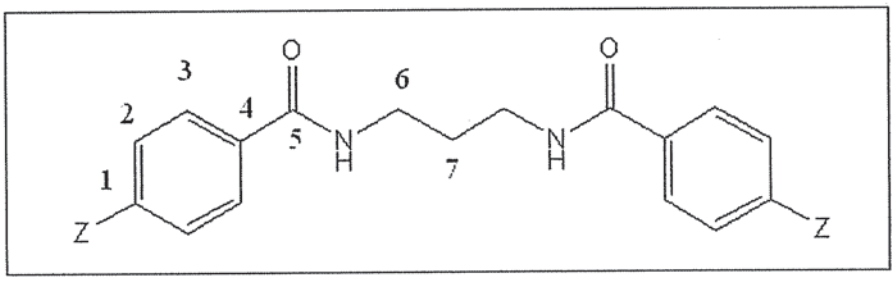



**Figure 4.3.** Principle carbon NMR signals of $B_1$ (100 MHz in $CDCl_3$)

**Table 4.10.** 100 MHz $^{13}C$ NMR spectrum of compound of bis-amide



| Compound ID | δ (ppm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | $C_1$ | $C_2$ | $C_3$ | $C_4$ | $C_5$ | $C_6$ | $C_7$ |
| $B_1$ | 142.0 | 129.3 | 127.1 | 131.5 | 168.3 | 36.2 | 30.0 |
| $B_2$ | 148.2 | 128.2 | 127.2 | 131.8 | 168.3 | 36.1 | 30.1 |
| $B_3$ | 146.7 | 128.8 | 127.1 | 131.8 | 168.2 | 36.1 | 30.1 |
| $B_4$ | 146.9 | 128.7 | 127.1 | 131.7 | 168.3 | 36.1 | 30.0 |
| $B_6$ | 146.9 | 128.7 | 127.1 | 131.8 | 168.3 | 36.1 | 30.1 |
| $B_7$ | 147.0 | 128.7 | 127.1 | 131.7 | 168.3 | 36.1 | 29.8 |
| $B_{10}$ | 147.0 | 128.7 | 127.1 | 131.7 | 168.2 | 36.1 | 30.1 |

## 4.3 STUDIES ON GELATION PROPERTIES OF $B_1$-$B_{10}$ DERIVATIVES IN ORGANIC SOLVENTS

### 4.3.1 Structure-property relationships on the gelation ability

The self-assembly process is affected by several factors like type of the solvents used in gelation, concentration of the organogelator, gelation temperature and especially molecular structure (e.g. electron density of aromatic part, types of functional groups, position of the substituting group etc.). It is known that variations in the structures or substituents allow us to understand the basis of the relation between aggregate gel properties and molecular structure.

DEMİR-ORDU and coworkers (2015) already observed that bis-carbamate based low molecular weight organogelators (1,3-bis[N-(p-aryl)-carbomoyloxy]propanes) can gelate common organic solvents like toluene, xylene; esters used in pharmaceutical industry like ethyl laurate, N-butyl palmitate, isopropyl myristate and vegetable oils like olive oil, corn oil and sunflower oil. The investigated bis-carbamate compounds include three different structural parts; two carbamate units that are able to form hydrogen bonds, an aryl moiety substituted by electron donating groups which may increase the strength of π-π stacking and aliphatic spacers of different lengths that can be involved in van der Waals interactions. The result showed that;

- The length of alkyl spacer
- The presence of *p*-alkyl or *p*-alkoxy groups and their chain length
- Concentration and
- Temparature affect the organogelation process.

The results from NMR and FTIR studies revealed that the self-assembly into fibrous structures is mainly driven by hydrogen bonding between carbamate units. π-π and van der Waals interactions were found to be the secondary forces in gel formation. The presence of three methylene groups between the carbamate groups also had an important role in organogelation. Besides, cryogels were obtained at -18°C.

With these results in hand, new bis-amide derivatives (N,N'-(propane-1,3-diyl)bis(4-*p*-benzamide), ($B_1$-$B_{10}$) were designed, and their organogelation properties were tested in organic solvents. The results were given in Figures 4.4-4.6 and Tables 4.11-4.13. Similar to the structure of bis-carmabates, they had two hydrogen bonding sites (amide unit), $\pi$-$\pi$ interaction site (N-aryl ring) and van der Waals interaction site (*p*-alkyl substituents). Therefore, gelation mechanism is expected to be the same with that of 1,3-bis[N-(p-aryl)-carbomoyloxy]propanes. However, the strength of hydrogen bonding is predicted to be stronger due to better hydrogen bonding ability of amide groups.

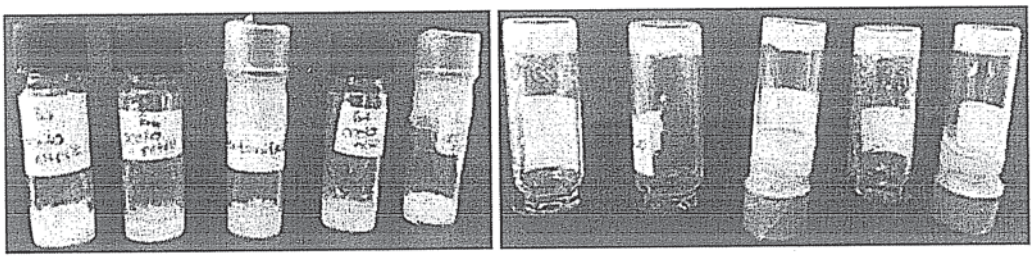


**Figure 4.4.** Organogel abilities in acetonitrile

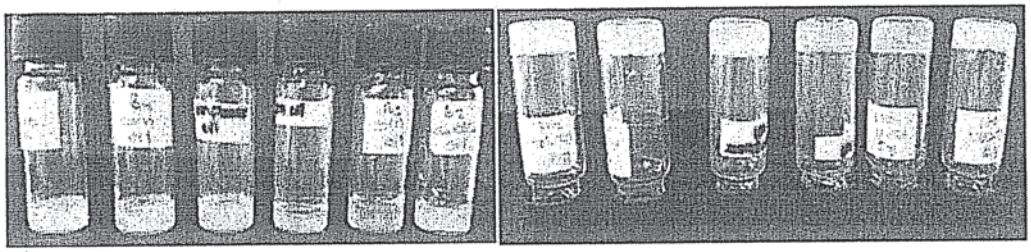


**Figure 4.5.** Organogel abilities in vegatable oils

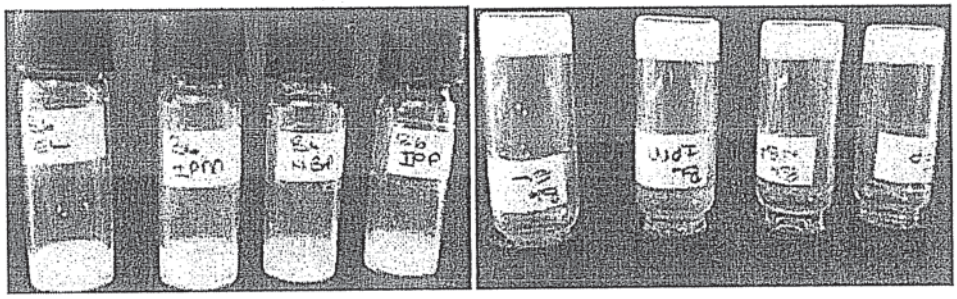


**Figure 4.6.** Organogel abilities in esters

**Table 4.11.** Organogelation behaviors of *p*-alkyl substituted derivatives $B_1$-$B_{10}$ in organic solvents

| NAME CODE | CONDITION RT/-18°C | DMSO | DCM | EtOH | TCM | TOLUENE | XYLENE | ACETONE | ACN | ETHYLACETATE |
|---|---|---|---|---|---|---|---|---|---|---|
| $B_1$ | RT | SOL | PG | SOL | SOL | PPT | PPT | PPT | GEL* (31.32mg) | PG |
| Z: Methyl | -18°C | SOL | PG | SOL | SOL | PPT | PPT | PPT | GEL | PG |
| $B_2$ | RT | SOL | SOL | SOL | SOL | PPT | PPT | PPT | GEL* (89.10mg) | PPT |
| Z: Ethyl | -18°C | SOL | SOL | SOL | SOL | PPT | PPT | PPT | GEL | PPT |
| $B_3$ | RT | SOL | SOL | SOL | SOL | PG | PG | PPT | GEL* (71.70mg) | PPT |
| Z: Propyl | -18°C | SOL | SOL | SOL | SOL | PG | PG | PPT | GEL | PPT |
| $B_4$ | RT | SOL | SOL | SOL | SOL | PPT | PPT | SOL | GEL* (36.84mg) | PPT |
| Z: Butyl | -18°C | SOL | SOL | SOL | SOL | PPT | PPT | SOL | GEL | PPT |
| $B_6$ | RT | SOL | SOL | SOL | SOL | PPT | PPT | PPT | GEL* (23.70mg) | PPT |
| Z: Hexyl | -18°C | SOL | SOL | SOL | SOL | PPT | PPT | PPT | GEL | PPT |
| $B_7$ | RT | PPT | SOL | PPT | SOL | PPT | PPT | PPT | GEL* (24.02mg) | PPT |
| Z: Heptyl | -18°C | PPT | SOL | PPT | SOL | PPT | PPT | PPT | GEL | PPT |
| $B_{10}$ | RT | PPT | SOL | PPT | SOL | PPT | PPT | PPT | GEL* (26.14mg) | PPT |
| Z: Decyl | -18°C | PPT | SOL | PPT | SOL | PPT | PPT | PPT | GEL | PPT |

RT: Room Temperature, SOL: Solution, PPT: Precipitate, PG: Partial Gel, DMSO: Dimethyl sulphoxide, DCM: Dichloromethane, EtOH: Ethanol, TCM: Chloroform, ACN: Acetonitrile (*mgc=mg/1 mL solvent)

**Table 4.12.** Organogelation behaviors of *p*-alkyl substituted derivatives $B_1$-$B_{10}$ in petroleum products and organic solvents

| NAME CODE | CONDITION RT/-18°C | 1-OCTANOL | 2-OCTANOL | 2-PROPANOL | GASSOLINE | EURO DIESEL | DIESEL | GAS OIL | VASELINE | GLYCERINE |
|---|---|---|---|---|---|---|---|---|---|---|
| $B_1$ Z:Methyl | RT | GEL* (44.90mg) | PG | GEL* (49.96mg) | SOL | INSOL | INSOL | INSOL | INSOL | INSOL |
| | -18°C | GEL | PG | GEL | SOL | INSOL | INSOL | INSOL | INSOL | INSOL |
| $B_2$ Z: Ethyl | RT | SOL | SOL | SOL | SOL | INSOL | INSOL | INSOL | GEL* (25.72mg) | GEL* (12.24mg) |
| | -18°C | SOL | SOL | SOL | SOL | INSOL | INSOL | INSOL | GEL | GEL |
| $B_3$ Z: Propyl | RT | SOL | SOL | SOL | SOL | INSOL | INSOL | PPT | GEL* (17.82mg) | PG |
| | -18°C | SOL | SOL | SOL | SOL | INSOL | INSOL | PPT | GEL | PG |
| $B_4$ Z: Butyl | RT | SOL | SOL | SOL | SOL | PPT | PPT | PPT | GEL* (10.70mg) | GEL* (20.40mg) |
| | -18°C | SOL | SOL | SOL | SOL | PPT | PPT | PPT | GEL | GEL |
| $B_6$ Z: Hexyl | RT | SOL | SOL | SOL | SOL | GEL* (44.88mg) | GEL* (46.34mg) | GEL* (22.64mg) | GEL* (32.12mg) | SOL |
| | -18°C | SOL | SOL | SOL | SOL | GEL | GEL | GEL | GEL | SOL |
| $B_7$ Z:Heptyl | RT | SOL | SOL | PPT | SOL | GEL* (34.08mg) | GEL* (49.20mg) | GEL* (32.26mg) | GEL* (20.86mg) | SOL |
| | -18°C | SOL | SOL | PPT | SOL | GEL | GEL | GEL | GEL | SOL |
| $B_{10}$ Z: Decyl | RT | PPT | PPT | PPT | SOL | PPT | PPT | GEL* (11.00mg) | GEL* (24.18mg) | SOL |
| | -18°C | PPT | PPT | PPT | SOL | PPT | PPT | GEL | GEL | SOL |

RT: Room Temperature, SOL: Solution, INSOL: Insoluble PPT: Precipitate, PG: Partial Gel (*mgc=mg/1 mL solvent)

**Table 4.13.** Organogelation behaviors of *p*-alkyl substituted derivatives $B_1$-$B_{10}$ in ester groups

| NAME CODE | CONDITION RT/-18°C | CORN OIL | OLIVE OIL | NUT OIL | CANOLA OIL | SUNFLOWER OIL | E-L | NBP | IPM | IPP |
|---|---|---|---|---|---|---|---|---|---|---|
| $B_1$ | RT | GEL* (20.60mg) | GEL* (35.82mg) | GEL* (35.80mg) | GEL* (30.24mg) | GEL* (21.42mg) | PG | PG | PG | PG |
| Z:Methyl | -18°C | GEL | GEL | GEL | GEL | GEL | PG | PG | PG | PG |
| $B_2$ | RT | GEL* (54.60mg) | GEL* (22.18mg) | GEL* (24.56mg) | GEL* (52.64mg) | GEL* (37.66mg) | GEL* (43.88mg) | GEL* (25.70mg) | GEL* (41.80mg) | GEL* (25.74mg) |
| Z: Ethyl | -18°C | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL |
| $B_3$ | RT | GEL* (52.02mg) | GEL* (44.54mg) | GEL* (35.72mg) | GEL* (39.34mg) | GEL* (43.24mg) | PG | GEL* (40.92mg) | PG | PG |
| Z:Propyl | -18°C | GEL | GEL | GEL | GEL | GEL | PG | GEL | PG | PG |
| $B_4$ | RT | GEL* (46.72mg) | GEL* (30.60mg) | GEL* (19.06mg) | GEL* (32.70mg) | GEL* (20.76mg) | GEL* (33.18mg) | GEL* (34.72mg) | GEL* (18.36mg) | GEL* (21.94mg) |
| Z: Butyl | -18°C | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL |
| $B_6$ | RT | GEL* (34.62mg) | GEL* (36.00mg) | GEL* (36.64mg) | GEL* (35.40mg) | GEL* (32.76mg) | GEL* (35.40mg) | GEL* (23.54mg) | GEL* (32.74mg) | GEL* (22.36mg) |
| Z: Hexyl | -18°C | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL |
| $B_7$ | RT | GEL* (33.02mg) | GEL* (41.78mg) | GEL* (32.70mg) | GEL* (33.56mg) | GEL* (31.40mg) | GEL* (54.86mg) | GEL* (21.40mg) | GEL* (44.54mg) | GEL* (42.56mg) |
| Z:Heptyl | -18°C | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL |
| $B_{10}$ | RT | GEL* (26.92mg) | GEL* (35.12mg) | GEL* (38.46mg) | GEL* (35.70mg) | GEL* (35.18mg) | GEL* (41.90mg) | GEL* (25.08mg) | GEL* (13.36mg) | GEL* (12.40mg) |
| Z: Decyl | -18°C | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL | GEL |

RT: Room Temperature, PG: Partial Gel, NBP: n-Butyl Palmitate, IPM: Isopropyl myristate, IPP: Isopropyl palmitate, E-L: Ethyl Laurate

(*:mgc, mg/1ml solvent)

The organogelation abilities of the compounds ($B_1$, $B_2$, $B_3$, $B_4$, $B_6$, $B_7$, and $B_{10}$) were tested in a variety of organic solvents like esters, vegetable oils, common organic solvents and petroleum products (Figures 4.4- 4.6 and Tables 4.11-4.13).

The influence of the length of alkyl chain on gelation was studied on *p*-alkyl substituted bis-amide derivatives. All compounds did not form organogels in dimethyl sulphoxide, ethanol, chloroform, acetone, ethyl acetate and 2-octanol (Tables 4.11,4.12). They either formed solution or precipitation during cooling process. On the other hand, they formed gels in many solvents, especially in vegetable oils, acetonitrile and esters used in pharmaceutical formulations (Tables 4.11,4.13). Increasing the length of *p*-alkyl chain from methyl to decyl increased gelation ability especially in polar acetonitrile and hence decreased the minimum gelation concentration. This is the result of an enhancement of van der Waals interactions as expected. Similarly, it was observed that gelation in isopropyl myristate (IPM) and isopropyl palmitate (IPP) was obtained for derivative $B_{10}$ with the lowest mgc value. However, in vegetable oils which are nonpolar in nature, short *p*-alkyl chains ($B_1$-$B_4$) gelated with lower mgc values. These results agree with the general view that gelation is a balance between prepicitation and solubility. It is apperent that the elongation of the *para*-alkyl chain lead to lower the gelation ability in non-polar solvents due to their higher solvophilicity, while it increases the gelation in polar solvents as a result of increasing the strength of van der Waals interactions.

### 4.3.2 Temperature effect on gelation

Temperature dependence of gel formation was also investigated for all compounds (Tables 4.11- 4.13). The hot solutions were kept at -18°C for 15 min and gel formation was visually observed and tested by the "inverse flow" method. For all compounds tested, no significant influence of temperature on gelation was observed. Minimum gelation concentration were the same at room temparature and at -18°C.

### 4.3.3 Phase Selective organogelation from oil/water

Materialization of phase selective gelation from water and organic solvent mixtures is valued but challenging. The cause might be that water competes for the hydrogen bonding sites in the gelator molecules, and ruining gelation.(J.W. Liu et al., 2011)

The results of many studies revealed that the van der Waals interaction between the alkyl chains and the intermolecular hydrogen bonding between the amide groups should be an important driving force for the formation of the organogels. Interestingly, we found that synthesized gelators are insoluble in water and have good gelation abilities in many organic solvents, especially in non-polar ones. The organic solvents which can form strong gels (having more solid character than the others) were selected for this application: $B_2$ in glycerine, $B_3$ in sunflower oil, B4 in vaseline, $B_6$ in IPM, $B_7$ in euro dizel, $B_{10}$ in gassoline. In a typical procedure, 0.5 mL organic solvent and 0.5 mL water were added in a sample vial, to which a weighed amount of the gelator was added. The gelator was then solubilized in this two-phase solution by heating. After cooling the mixture to room temperature the organic layer was gelated selectively, and the water layer remained intact in liquid state (Figure 4.7). Furthermore, when the vial was gently shaken, the organic layer and the water layer were separated unmixed (Figure 4.8). The results showed that these materials in the form of "solidifier" may have an application for the removal of vegetable/petroleum oil spills from water.

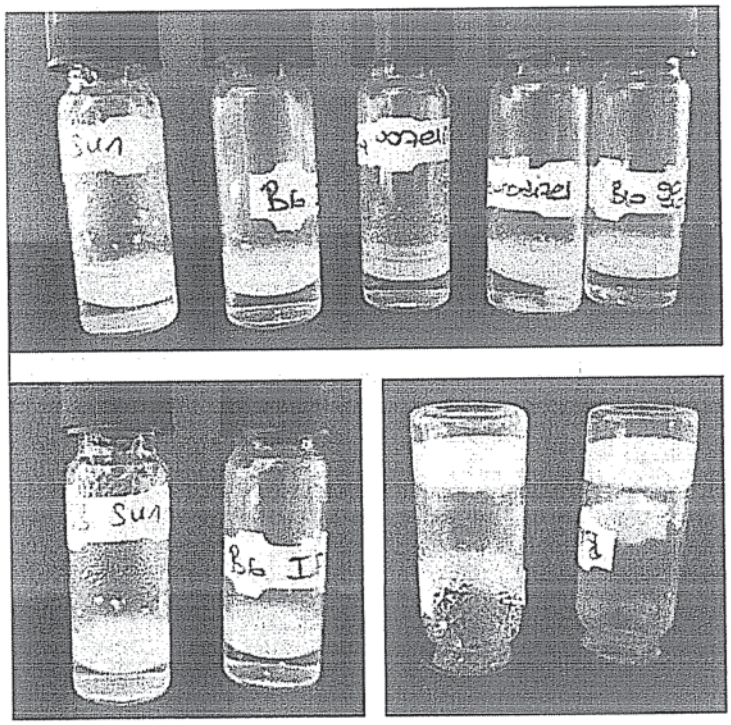


**Figure 4.7.** Phase selective organogelation ability

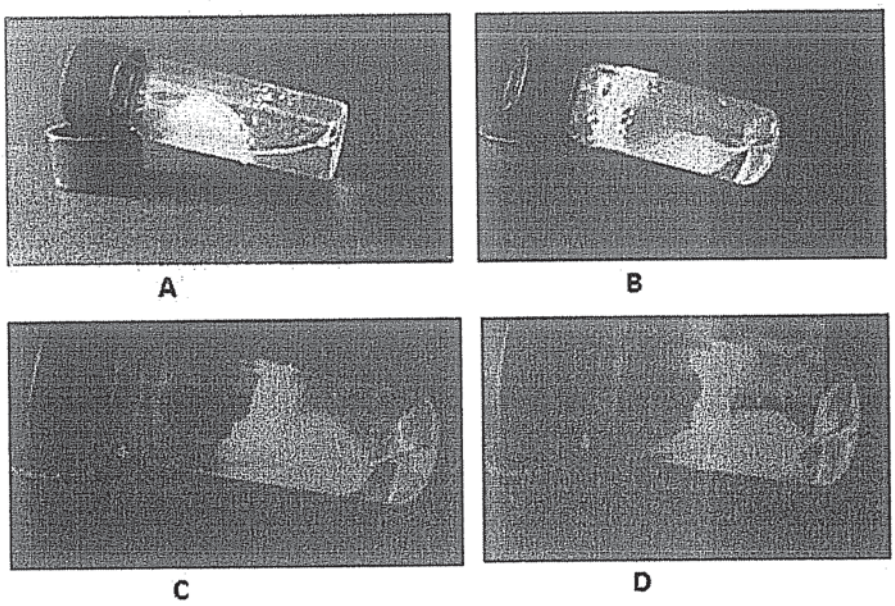



**Figure 4.8.** Selective removal from water **A:** $B_7$ in eurodizel, **B:** $B_4$ in vaseline, **C:** $B_{10}$ in gas oil, **D:** $B_6$ in IPM

Another application field is the usage of xerogels as nano-fibrous and porous sorbents. Oil spills considered as one of the most earnest disasters that are

threathening the marine ecosystem which are usually related to accidents in oil production, storage, and transportation. As long as fossil fuels are needed, oil spills are still a big problem that human beings are facing. (Zhu et al., 2013)

For this reason, it is essential to solve this environmental problem. There are many ways for oil spill cleanup methods like chemical, biological, and physical. (Wang et al, 2012)

Organogels are the lower-density, semi solid materials. They are also highly porous and capable of bearing weight many times their own.

Interestingly, we found that xerogels displayed remarkable abilities to entrap the oil part inside the porous or fibrous structure. This application has been tried for all derivatives in selected solvents. The results obtained are tabulated in Table 4.14. For this application, the gels obtained from volatile organic solvents were used. In a typical procedure, corn oil colored with methyl orange indicator was dropped into a beaker containing pure water. The weighed amount of the xerogel was left in the middle of the oil. Due to the adsorption of the colored oil the white xerogel became orange at the end. Then the oily gel could easily be removed from the water by means of a spatula (Figures 4.9- 4.11).

The oil absorbency (Q) was calculated with the equation (Table 4.14) used by Pourjavadi and his cowokers (2012) in an oil removal experiment. The oil absorbency was the best observed for $B_7$ derivative while the value for $B_2$ derivative was the worst. All the results obtained for the oil removal experiment are shown in Table 4.14.

**Table 4.14.** Oil removal experiments for the compounds in corn oil

| Compound ID | $W_{dry}$,Xerogel (mg) | $W_{wet}$, Oil + Gel (mg) | Q* |
|---|---|---|---|
| $B_1$ | 4.45 | 31.20 | 6.01 |
| $B_2$ | 5.00 | 5.63 | 0.13 |
| $B_3$ | 1.66 | 10.66 | 5.42 |
| $B_4$ | 2.16 | 11.65 | 4.39 |
| $B_6$ | 3.48 | 30.89 | 7.88 |
| $B_7$ | 2.00 | 25.03 | 11.52 |
| $B_{10}$ | 1.04 | 5.68 | 4.46 |

*: $Q=(W_{wet}-W_{dry})/W_{dry}(mg\ mg^{-1})$

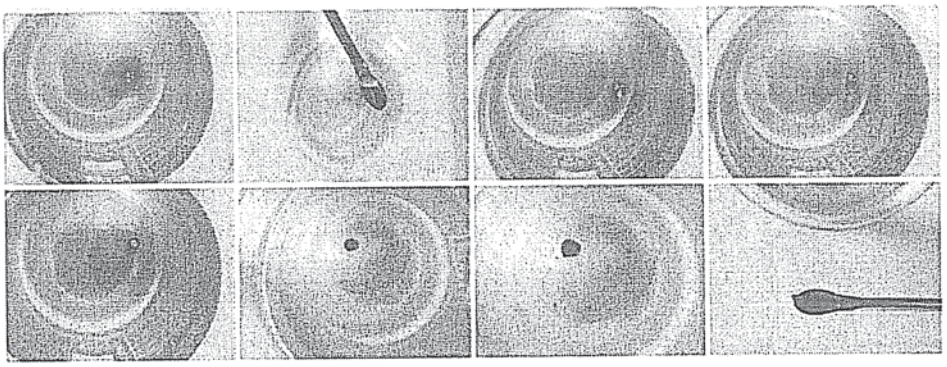


**Figure 4.9.** Oil removal of $B_1$ derivative in corn oil

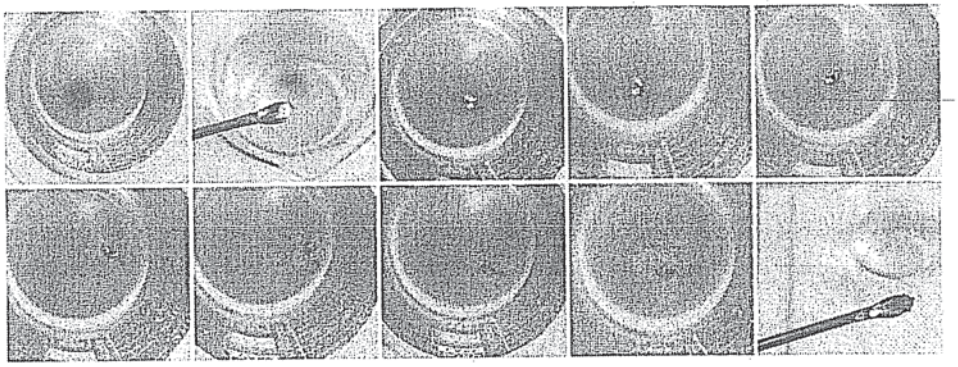


**Figure 4.10.** Oil removal of $B_3$ derivative in corn oil

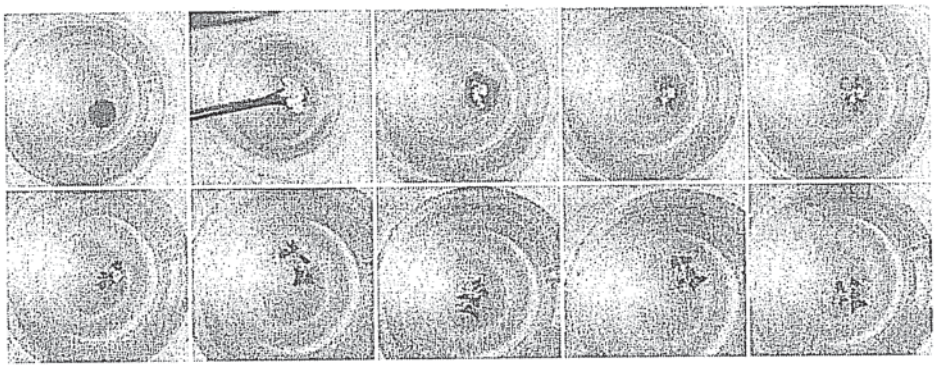


**Figure 4.11.** Oil removal of $B_6$ derivative in corn oil

### 4.3.4 Light Microscope Results

The morphology of gels were examined by optical microscopy. For this purpose, a certain amount of gel was taken and put on a lam and heated until it became a solution. Then it was allowed to cool to room temperature. During cooling morphologies were studied using optical microscope with 4x, 10x, 20x and 50x lenses. Figures 4.12 and 4.13 shows the optical micrographs of $B_6$-nut oil and $B_7$ n-butyl palmitate gels, respectively during the gel formation process. At the beginning there was only the solution because of the hot solution. Upon cooling self-assembly occured and 3D network formed.

Light microscopy studies proved that gelation took place through the entanglement of the brached fibers producing spaces for confining the solvent molecules (Figure 4.12-4.14).

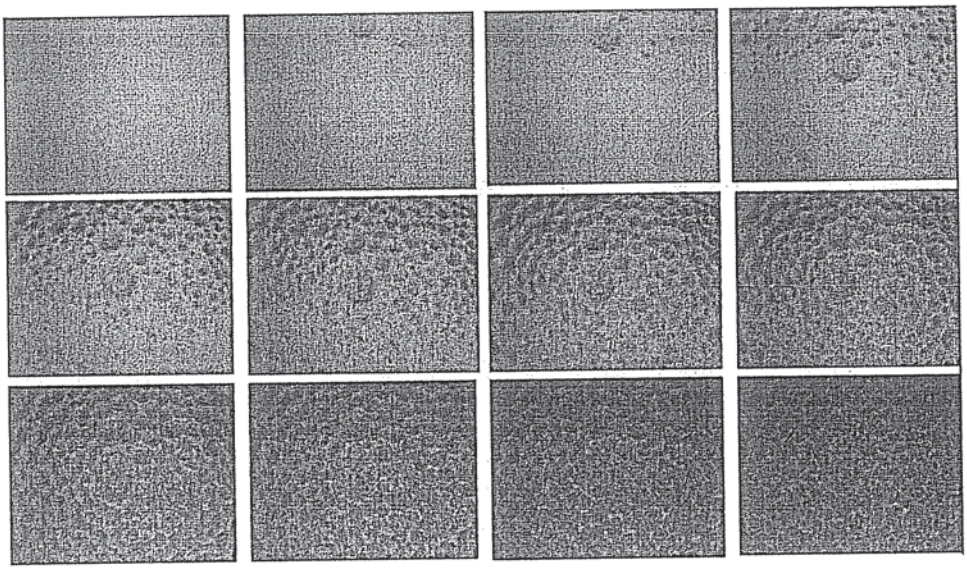


**Figure 4.12.** $B_6$ derivative in nut oil with 4x lens

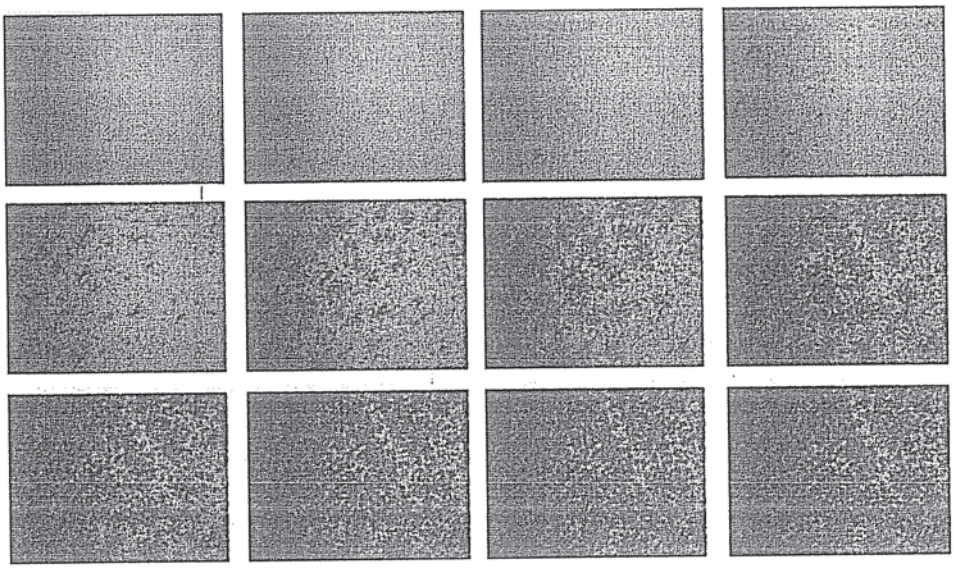


**Figure 4.13.** $B_7$ derivative in n-butyl palmitate with 4x lens

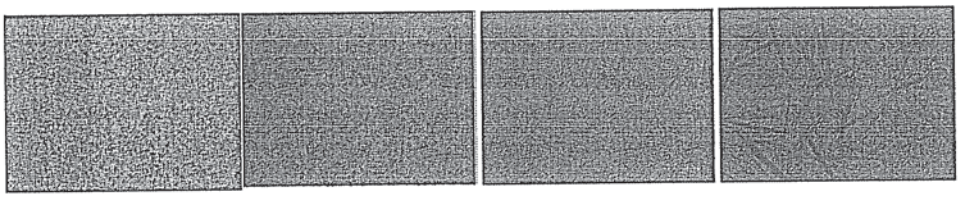
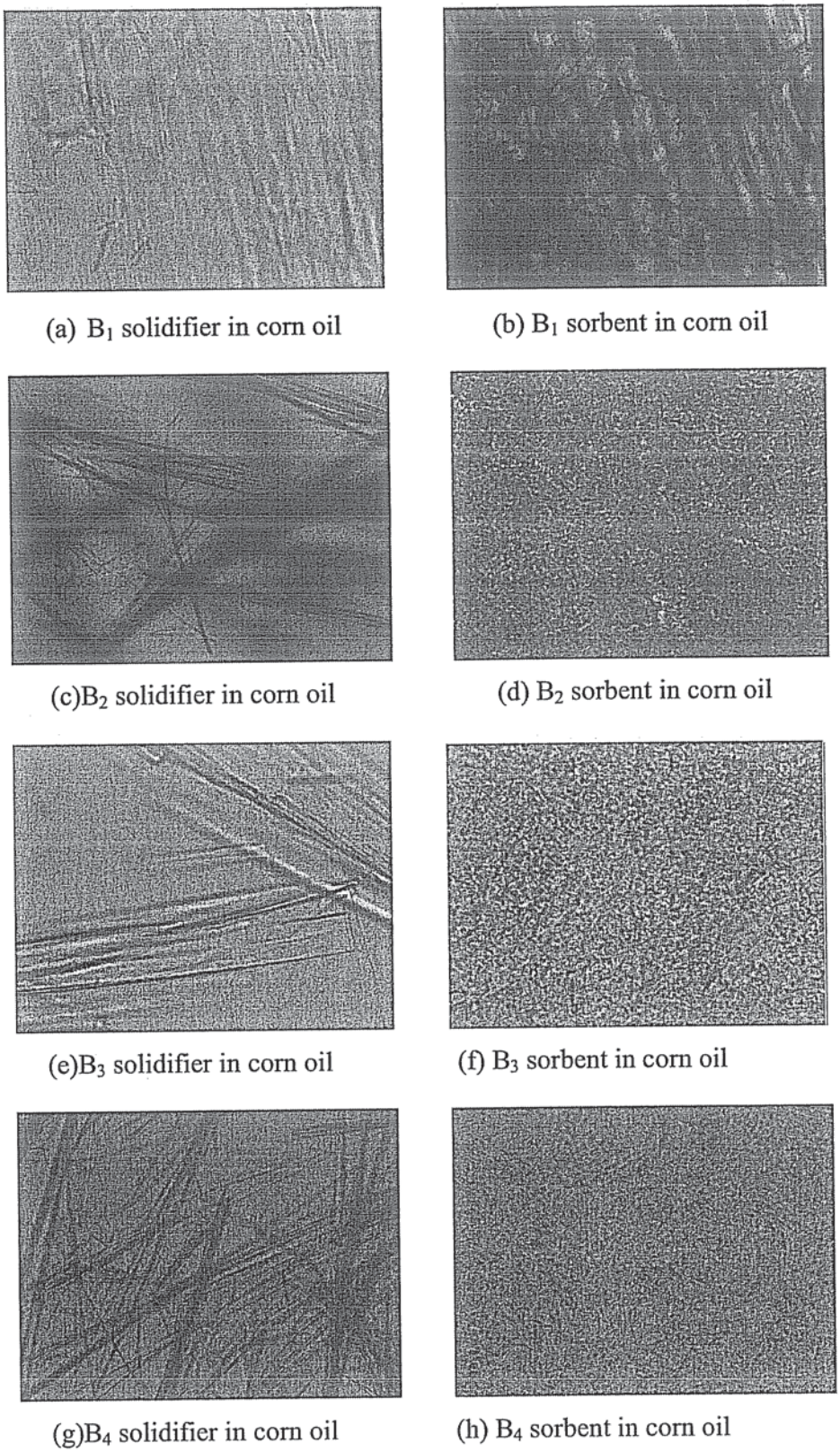


**Figure 4.14.** Optical micrographs of $B_{10}$-corn oil gel (a)4x, (b)10x, (c)20x, (d)50x magnifications

Similar fiber network formation was observed for all derivatives used as both solidifiers and sorbents in corn oil (Figure 4.15).



(a) $B_1$ solidifier in corn oil

(b) $B_1$ sorbent in corn oil

(c)$B_2$ solidifier in corn oil

(d) $B_2$ sorbent in corn oil

(e)$B_3$ solidifier in corn oil

(f) $B_3$ sorbent in corn oil

(g)$B_4$ solidifier in corn oil

(h) $B_4$ sorbent in corn oil

**Figure 4.15.** Optical micrographs with 20x magnification showing the usage of the compounds as solidifiers and sorbents in corn oil

# 5 CONCLUSION

In this current work, new bis amide derivatives were obtained efficiently. Synthesis of bis (*p*-aryl) amide derivatives ($B_1$-$B_{10}$) were carried out by the reaction of benzoyl chloride and 1,3-diaminopropane with a yield of 83-91%. Structures of the compounds ($B_1$-$B_{10}$) were determined by IR, $^1H$ and $^{13}C$ NMR spectroscopy.

Organogelation properties of bis-amide derivatives were tested in common organic solvents (toluene, xylene, etc.), vegetable oils (sunflower oil, olive oil, etc.), petroleum products (gassoline, diesel, euro diesel) and ester used in pharmaceutical applications (n-butyl palmitate, ethyl laurate, etc.) by test tube inversion method.

It was found that the type of substituent on the *para* position (*p*-alkyl) and the length of the alkyl chain affected the organogelation properties. The elongation of the *para*-alkyl chain lead to lower the gelation ability in non-polar solvents due to their higher solvophilicity, while it increases the gelation in polar solvents as a result of increasing the strength of van der Waals interactions.

Phase selectivities of the resulting organogels were examined by performing oil removal experiments. The results showed that these materials in the form of "solidifier" may have an application for the removal of vegetable/petroleum oil spills from water.

Xerogels were also found to display remarkable abilities to entrap the oil part inside the porous or fibrous structure. This application has been tried for all derivatives in selected solvents. The oil absorbance was the best observed for $B_7$ derivative while the value for $B_2$ derivative was the worst.

Light microscopy studies proved that gelation took place through the entanglement of the brached fibers producing spaces for confining the solvent molecules.

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# 7 CURRICULUM VITAE


| | | |
|---|---|---|
| **Name SURNAME** | : | Burcu BİLALOĞLU |
| **Place and Date of Birth** | : | Pazar/RİZE 15/03/1990 |
| **Universities** | | |
| **- Bachelor's Degree** | : | Kocaeli University |
| **- Bachelor's Degree** | : | Abant İzzet Baysal University |
| **e-mail** | : | burcu.bilaloglu.3@gmail.com |
| **Adress** | : | Karamanlı Mah. Mutlu Sok. No:13/16 Merkez / BOLU |