Molten Tetrabutylammonium Bromide as Eco-Friendly Media for the Synthesis of Optically Active and Thermal Stable Polyamides under Microwave Irradiation

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The present paper is an extension of microwave method describing the synthesis of optically active polyamides (**PA**s). The main focus of this work is the design of effective microwave method for preparing of optically active **PA**s. The diacid containing amino acid and 1,8-naphthalimide group was prepared in three steps. For the preparation of optically active polymers from this monomer the polycondensation reactions of diacid 7 with different aromatic and aliphatic diisocyanates was employed in the presence of a small amount of tetrabutylammonium bromide as ionic liquid media that acts as a primary microwave absorber and was compared with conventional heating. The resulting polymers were characterized using FT/IR, ^{1}H NMR, ^{13}C NMR, UV-vis spectroscopy, fluorimetry, specific rotation techniques and elemental analysis. Thermal properties of the resulting **PA**s were evaluated by thermogravimetric analysis and differential scanning calorimetry. The interpretation of kinetic parameters (E, ΔH, ΔS and ΔG) of thermal decomposition stages have also been evaluated using Coats-Redfern and Dharwadkar-Kharkhanawala equations.

KEY WORDS: Green Chemistry / Optically Active Polymers / Ionic Liquids / Thermal Properties / Kinetic Study / Microwave-Assisted Polycondensation /

Due to worsening of the environment, green chemistry has been receiving progressively more attention since the 1990's.[1,2] Hence, there is a great necessitate for the advancement of novel methodologies for polymerization using environmentally eco-friendly media and give sufficient solubility to polymerization which could replace the highly polar conventional and chlorinated solvents which are volatile, most of them flammable, toxic, quite hazardous and harmful.[3–6] Ionic liquids (**IL**s) made of organic cations and suitable anions have attracted much recent consideration as solvents for chemistry because of the fact that they have melting points close or near to room temperature. The most of **IL**s are clear and colorless viscous liquid. **IL**s possess a distinctive array of physico-chemical properties that make them appropriate in numerous task-specific uses in which conventional solvents are non-applicable or ineffectually effective. Such properties comprise: high electrical conductivity, high thermal stability, large electrochemical window, low nucleophilicity and capability of providing weekly coordinating or noncoordinating environment, very good solvents properties for a broad diversity of inorganic, organic, organometallic and polymeric compounds.[7–12] In some cases, the solubility of certain solutes in **IL**s can be some orders of magnitude higher than that in traditional solvents. However, the high cost of most room temperature **IL**s and apprehension about their toxicity has led researchers to find out the use of more benign salts in the molten state as useful alternatives. Recently, molten tetrabutylammonium bromide (TBAB) was used as a low toxic and cost-effective **IL** in a number of constructive synthetic transformations.[13–15]

The synthesis and application of optically active polymers have recently become the focus of greater attention because polymers with chiral structures are biologically very important. Most of the natural polymers are optically active and have special chemical activities such as catalytic properties that exist in proteins, enzymes, and genes.[16–24]

The application of microwave energy for the synthesis of organic compounds has been used since 1986. Microwave ovens are a feature of many households, but in the industrial world, microwave energy has been applied to several areas, including bulk food processing, the drying and curing of paper and wood products, the vulcanization of rubber and the drying of thermoplastics before extrusion. Also the mechanism of microwave heating is independent of the thermal conductivity, microwave heat the molecules directly through the interaction between microwave energy and molecular dipole moments of the monomers containing polar groups and ionic solvents that favor the absorption of microwaves and avoids the heat-transfer rate problem encountered in conventional thermal heating. In polymer processing, to merge the advantages of microwave techniques and **IL**s for more sophisticated processing and fabrication of polymers several organic reactions such as acetylation, oligomerization, dimerization, polymerization and copolymerization reactions have been carried out in **IL** under microwave irradiation.[25–34]

Chromophoric polymers have been widely explored in the last decade due to their potential technological use in electronic devices and opto-electronic. Naphthalene structure as a chromophore gave special features such as bulky, rigid,

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moisture resistance and low coefficient of thermal expansion to polymer. Naphthalene has also been incorporated into the backbones of many polymers including **PA**s, polyesters, bismaleimides and etc. The amalgamation of naphthalene as a pendant group in a polymer chain has resulted in decreased crystallinity and enhanced solubility and thermal stability.[35–38]

Recently, much attention on high-performance polymers that have excellent thermal stability and solubility has provided researchers with the impetus that has led to the discovery of a variety of processable and thermostable polymers. **PA**s are one of the high-performance polymeric materials and are characterized by thermo oxidative stability and high thermal, good mechanical properties, and outstanding solvent resistance. However, poor solubility is a major problem for wide application of **PA**s, but these inherent problems have been dealt by many research efforts during the last decades by incorporation of alkyl or aryl substitution to decrease the hydrogen bonding at the amide linkage, symmetric/asymmetric bulky substitution in the aromatic rings, copolymerization, lateral substituents, nature of parent chain in the polymer forming monomeric units, noncoplanar biphenylene moieties, pendant phenyl group and flexible alkyl spacers into the **PA**s backbone.[39–44]

1,8-naphthalimide moieties have become a very actual class of organic luminophores, on the other hand polymers containing this functional group can be used as sensors for transition metal ions or protons whose sensor characteristics can be explained either by conformational changes in the macromolecules or by the collective transport properties. In this study, we wish to report a combination of microwave energy with **IL**s as reaction media under green conditions for the synthesis of optically active and photolabeling **PA**s containing 1,8-naphthalenedicarboxylic anhydride and S-valine as pendant moieties and compares it with classical heating solution polymerization. In another section of this research we set out to investigate kinetic study and thermal decomposition behavior of these **PA**s.

EXPERIMENTAL

Materials

Reagents were purchased from Fluka Chemical (Buchs, Switzerland), Aldrich Chemical (Milwaukee, WI) and RiedeldeHaen AG (Seelze, Germany). *N,N*-Dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP) were dried over BaO and then were distilled under reduced pressure. 5-Aminoisophthalic acid (6) was recrystallized from H_2O/DMF (*N,N*-dimethylformamide) (4/1) mixture. 1,8-Naphthalenedicarboxylic anhydride was recrystallized from hot acetic anhydride. 1,4-Diazabicyclo[2.2.2]octane (DABCO) and tetrabutylammoniom bromide (TBAB) were purchased from Merck Co. and were used without further purification.

Techniques

^{1}H NMR (500 MHz) spectra were recorded on a Bruker (Germany), Avance 500 instrument. FT/IR spectra were recorded on (Jasco-680, Japan) spectrophotometer. Spectra of solids were carried out using KBr pellets. All melting points were taken with a Gallenham melting point apparatus. The microwave apparatus used for the polycondensation was a Samsung (Seoul, South Korea) microwave oven (2450 MHz and 900 W). Inherent viscosities were measured by standard procedure using a Cannon Fenske Routine viscometer. Quantitative solubility was determined using 0.05 g of the polymer in 1 mL of solvent. Elemental analyses were performed by Research Institute of Polymer and Petrochemical of Iran (IPPI). Fluorescence and UV-vis spectra were recorded on a spectrofluorometer, JASCO, FP-750 and UV/Vis/NIR spectrophotometer, JASCO, V-570, respectively. Thermal gravimetric analysis (TGA) data for polymers were taken on a TGA-Perkin Elmer (Pyris 1) at a heating rate of 10 °C min under N_2 atmosphere and differential scanning calorimetry (DSC) data were recorded on a DSC-PL-1200 instrument under N_2 atmosphere by IPPI.

Monomer Synthesis

5-[3-methyl-2-(1,8-naphthalimidyl)butanoylamino]isophthalic acid (6) was prepared (Scheme 1) according to our previous work.[45]

Polymer Synthesis

Method I. Polymerization of diacid 7 with diisocyanates in TBAB as an **IL** media under conventional heating.

A typical preparation of **PA9** is as follow: A 25 mL round-bottomed flask equipped with a mechanical stirrer was charged with a mixture of compound 7 (0.10 g, 2.17×10^{-4} mol), triethylamine (TEA) (0.02 mL, 1.80×10^{-4} mol) and TBAB (0.30 g, 9.42×10^{-4} mol) was ground until a powder was formed then toluylene-2,4-diisocyanate TDI (9) (0.04 g, 2.17×10^{-4} mol) was added. The mixture, blanketed by nitrogen, was stirred and heated to 120 °C for 12 h. The viscous final solution was poured in 30 mL of methanol to precipitate the polymer. The white solid was washed thoroughly with water. The resulting polymer was dried in a vacuum oven at 80 °C, yielded 0.12 g (86%) of **PA9**. All others **PA**s were also synthesized with a similar procedure, using pyridine (Py), tributylamine (TBA), DABCO, DBTDL as catalysts and without any catalyst, respectively.

Method II. Polymerization of diacid 7 with diisocyanates in TBAB as an **IL** media under microwave irradiation.

The **PA**s were prepared by the following general procedure (taking **PA21** as an example): Into a porcelain dish, TBAB (0.23 g, 6.98×10^{-4} mol) and monomer 7 (0.10 g, 2.36×10^{-4} mol) were added. After the mixture was completely ground, DBTDL (0.02 g, 3.01×10^{-5} mol) was added and the mixture was ground for 10 min, then TDI (9) (0.04 g, 2.36×10^{-4} mol) was added and the mixture was ground again for additional 2 min. The reaction mixture was irradiated in a microwave oven for 1 min then it was cooled and irradiated for 30 more s at 100% (900 W) of its power level. The resulting product was isolated by the addition of 30 mL of methanol. It was then filtered off and dried at 80 °C for 7 h in vacuum, this yielded 0.13 g (89%) of white **PA21**. The above polymerization was

Scheme 1.
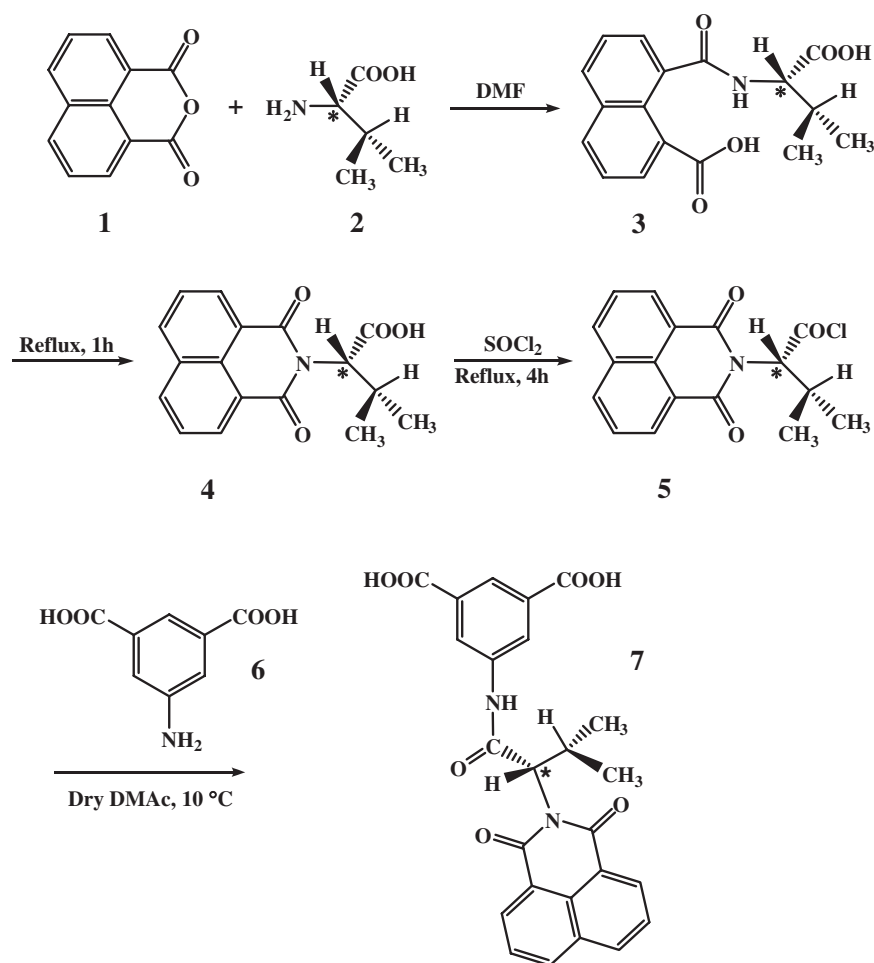
also repeated and the reaction mixture was irradiated in a microwave oven using Py, TEA, TBA and DABCO as catalysts, and without any catalyst, respectively. For each method, the optimized reaction conditions according to reaction time and reaction catalysts were selected for the polymerization of diacid monomer 7 with other diisocyanates such as 4,4′-methylenebis(phenyl isocyanate) MDI (8), isophorone diisocyanate IPDI (10) and hexamethylene diisocyanate HDI (11).

PA2. FT/IR (KBr, cm^{-1}): 3317 (w), 3109 (w), 2965 (w), 1702 (m), 1662 (s), 1590 (s), 1509 (s), 1436 (w), 1409 (m), 1379 (m), 1340 (m), 1312 (m), 1238 (m), 1200 (w), 1103 (w), 1018 (w), 909 (w), 845 (w), 781 (w), 754 (w). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.73 (d, 3H, CH$_3$, $J = 5.05$ Hz), 1.24 (d, 3H, CH$_3$, $J = 4.90$ Hz), 2.84 (m, 1H, CH), 3.87 (s, 2H, CH$_2$), 5.31 (d, 1H, CH, $J = 8.35$ Hz), 7.19 (d, 2H, CH, $J = 7.20$ Hz), 7.66 (d, 2H, CH, $J = 7.40$ Hz), 7.91 (s, 2H, CH), 8.14 (s, 1H, CH), 8.26 (s, 2H, CH), 8.54 (dd, 2H, CH, $J_1 = 16.05$ Hz, $J_2 = 6.60$ Hz), 9.95 (s, 1H, NH), 10.35 (s, 1H, NH). UV (DMF): λ_{max} (ε) 264 (40833.33), 335 nm (20416.3 L mol^{-1} cm^{-1}).

PA8. FT/IR (KBr, cm^{-1}): 3317 (m), 3073 (m), 2955 (m), 2924 (s), 2850 (s), 1707 (m), 1665 (s), 1588 (s), 1554 (s), 1432 (s), 1377 (m), 1343 (m), 1281 (w), 1239 (w), 1188 (w), 1153 (w), 1108 (m), 1072 (m), 1027 (w), 909 (s), 842 (s), 780 (m), 747 (s), 712 (s), 679 (w), 618 (w), 548 (w), 495 (w). Elemental analysis calculated for C$_{35}$H$_{37}$N$_4$O$_5$ (593.69 g/mol): C, 70.81%; H, 6.28%; N, 9.44%. Found: C, 70.64%; H, 6.31%; N, 9.37%. UV (DMF): λ_{max} (ε) 264 (16527.78), 335 nm (20416.3 L mol^{-1} cm^{-1}).

PA12. FT/IR (KBr, cm^{-1}): 3305 (s), 3070 (w), 2921 (s), 2851 (s), 1702 (s), 1665 (s), 1633 (s), 1589 (m), 1541 (s), 1466 (w), 1433 (w), 1378 (m), 1342 (m), 1276 (w), 1235 (m), 1185 (w), 1107 (w), 1028 (w), 934 (w), 909 (w), 844 (w), 779 (m), 744 (w), 687 (w), 587 (w), 541 (w), 497 (w), 476 (w). ^{1}H NMR (500 MHz, DMSO-d_6): δ 0.71 (d, 3H, CH$_3$, $J = 5.17$ Hz), 1.23 (d, 3H, CH$_3$, $J = 5.59$ Hz), 1.22–1.31 (m, 12H, CH$_2$), 2.82 (m, 1H, CH, $J = 6.40$ Hz), 5.27 (d, 1H, CH, $J = 8.06$ Hz), 8.00 (s, 2H, CH), 8.11 (s, 1H, CH), 8.41 (s, 2H, CH), 8.57 (t, 4H, CH, $J = 11.18$ Hz), 9.77 (s, 2H, NH), 9.85 (s, 1H, NH). UV (DMF): λ_{max} (ε) 264 (13611.11), 335 nm (20416.3 L mol^{-1} cm^{-1}).

PA22. FT/IR (KBr, cm^{-1}): 3311 (s), 3115 (w), 2922 (s), 2851 (s), 1714 (s), 1663 (s), 1654 (s), 1587 (m), 1560 (s), 1436 (w), 1379 (m), 1347 (m), 1269 (w), 1239 (m), 1184 (w), 1135 (w), 1106 (w), 1024 (w), 903 (m), 842 (w), 778 (s), 746 (w), 685 (w), 624 (w), 597 (w), 539 (w), 497 (w), 473 (w). Elemental
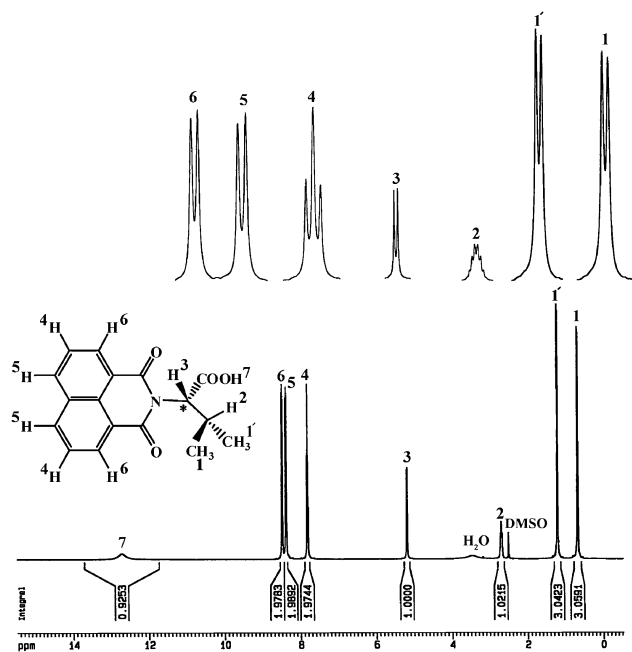
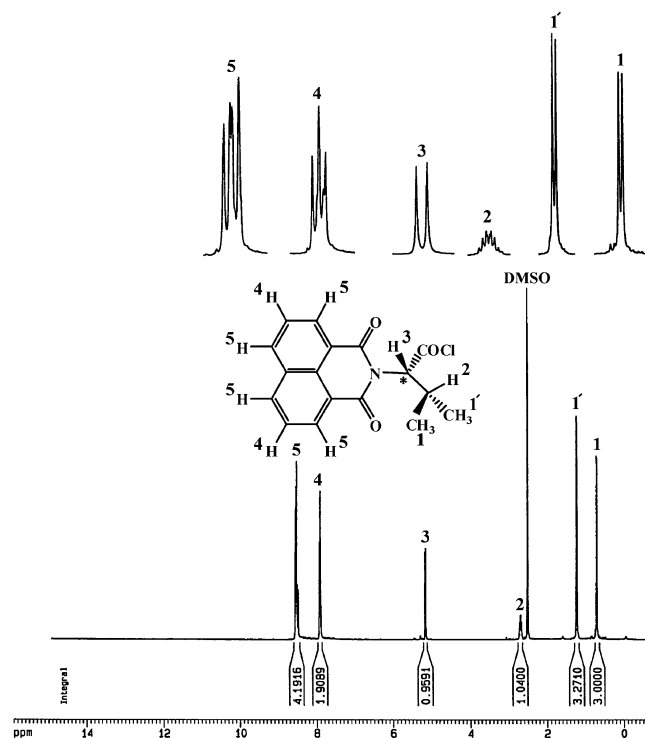**Figure 1.** ^{1}H NMR (500 MHz) spectrum of imide acid 4 in DMSO-d_6 at R.T.

Figure 2. ^{1}H NMR (500 MHz) spectrum of acid chloride 5 in DMSO-d_6 at R.T.

Table I. ^{1}H NMR and elemental analysis data of compounds 4, 5 and 7

Compound	Spectra data	
4	^{1}H NMR (500 MHz, DMSO-d_6): δ 0.67 (d, 3H, CH$_3$, J = 6.83 Hz), 1.21 (d, 3H, CH$_3$, J = 6.38 Hz), 2.70 (m, 1H, CH), 5.18 (d, 1H, CH, J = 9.13 Hz), 7.82 (t, 2H, CH, Ar-H), 8.39 (d, 2H, Ar-H, J = 8.16 Hz), 8.48 (d, 2H, Ar-H, J = 7.19 Hz), 12.71 (s, 1H, COOH) ppm.	^{13}C NMR (500 MHz, DMSO-d_6): δ 171.52 (C, COOH), 164.17 (C, C=O), 135.62 (CH, Ar), 132.22 (CH, Ar), 132.06 (C, Ar), 128.16 (CH, C, Ar), 122.07 (C, Ar), 58.82 (CH), 27.81 (CH), 23.00 (CH$_3$), 19.77 (CH$_3$) ppm.
5	^{1}H NMR (500 MHz, DMSO-d_6): δ 0.70 (d, 3H, CH$_3$, J = 6.93 Hz), 1.21 (d, 3H, CH$_3$, J = 8.03 Hz), 2.69 (m, 1H, CH), 5.17 (d, 2H, CH, J = 9.21 Hz), 7.92 (t, 2H, CH, Ar-H), 8.54 (dd, 2H, Ar-H, J_1 = 8.22 Hz, J_2 = 8.35 Hz) ppm.	
7	^{1}H NMR (500 MHz, DMSO-d_6): δ 0.71 (d, 3H, CH$_3$, J = 6.35 Hz), 1.23 (d, 3H, CH$_3$, J = 5.90 Hz), 2.81 (m, 1H, CH), 5.30 (d, 2H, CH, J = 8.45 Hz), 7.91 (t, 2H, CH, Ar-H), 8.13 (s, 1H, CH, Ar-H), 8.40 (s, 2H, CH, Ar-H), 8.52 (d, 2H, Ar-H, J = 8.06 Hz), 8.56 (d, 2H, Ar-H, J = 6.71 Hz), 9.95 (s, 1H, NH), 13.25 (s, 1H, COOH) ppm.	^{13}C NMR (500 MHz, DMSO-d_6): δ 168.83 (C, C=O), 167.39 (C, COOH), 164.69 (C, C=O), 140.62 (C, Ar), 135.50 (CH, Ar), 132.29 (CH, Ar), 132.24 (C, Ar), 132.08 (C, Ar), 128.52 (CH, Ar), 128.22 (C, Ar), 125.39 (CH, Ar), 122.86 (CH, Ar), 59.54 (C, Ar), 27.58 (CH), 23.29 (CH$_3$), 19.47 (CH$_3$) ppm.

analysis calculated for C$_{32}$H$_{26}$N$_4$O$_5$ (546.57 g/mol): C, 70.32%; H, 4.79%; N, 10.25%. Found: C, 69.74%; H, 5.24%; N, 10.17%. UV (DMF): λ_{max} (ε) 264 (96027.85), 335 nm (33348.40 L mol^{-1} cm^{-1}).

RESULTS AND DISCUSSIONS

Monomer Synthesis

Diacid 7 was prepared by the three-step process shown in Scheme 1.[45] 1,8-Naphthalenedicarboxilic anhydride (1) was allowed to react with S-valine (2) in DMF to provide imide acid 4. This compound was reacted with thionyl chloride to give corresponding acid chloride 5. The ^{1}H NMR spectra of compounds 4 and 5 showed all the peaks which were in good

agreement with the proposed structure (Figures 1 and 2) and the results are shown in Table I. This acid chloride was reacted with 5-aminoisophthalic acid (6) and diacid 7 was obtained in good yield. The ^{1}H NMR spectrum of diacid 7 showed all the peaks which were in good agreement with the proposed structure of compound 7 (Table I). The chemical structures and purities of compounds 4, 5 and 7 were proved with thin-layer chromatography, elemental analyses, FT/IR, specific rotation measurements, and ^{1}H NMR and ^{13}C NMR spectroscopy techniques.[45]

Polymer Synthesis

Since the appearance of microwave assisted synthesis in 1986, this technique has been recognized as a well-known
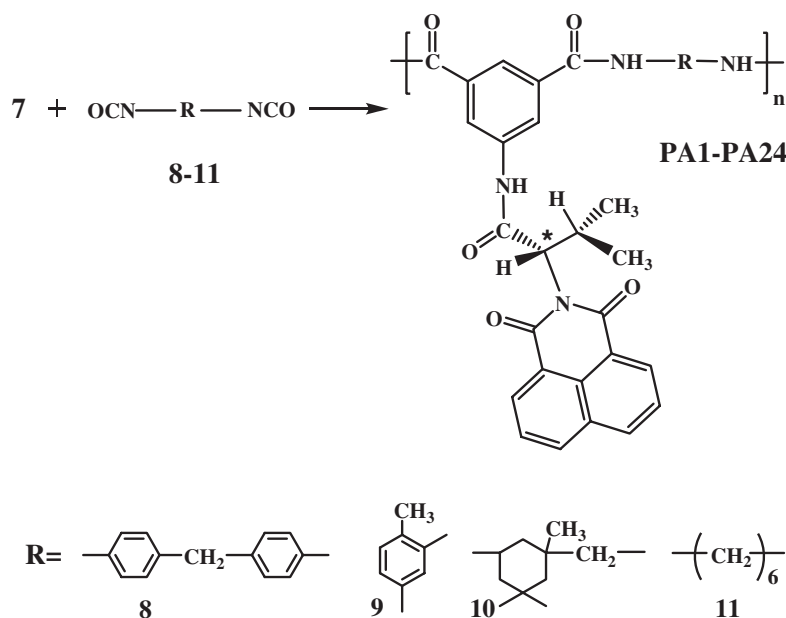
Scheme 2.

Table II. Reaction conditions for the polymerization of diacid 7 with different diisocyanates and some physical properties of **PA1-PA12** prepared by method I[a]

Polymer	Diisocyanate	Catalyst	Non-solvent	Yield (%)	η_{inh}[b] (dL/g)	$[\alpha]_D^{25}$[c]	$[\alpha]_{Hg}^{25}$ [c]
PA1	MDI	TEA	MeOH/Water	82	0.49	−30.14	−44.34
PA2	MDI	No cat	MeOH/Water	72	0.43	−34.22	−48.92
PA3	MDI	Py	MeOH/Water	74	0.49	−23.14	−47.65
PA4	MDI	DBTDL	MeOH/Water	77	0.49	−42.47	−44.68
PA5	MDI	TBA	MeOH/Water	74	0.45	−28.74	−41.54
PA6	MDI	DABCO	MeOH/Water	74	0.44	−44.87	−59.32
PA7	IPDI	TEA	Water	83	0.43	−24.17	−36.14
PA8	IPDI	No Cat	Water	75	0.30	−53.31	−65.10
PA9	TDI	TEA	Water	86	0.49	−35.97	−38.01
PA10	TDI	No Cat	Water	86	0.49	−23.01	−24.98
PA11	HDI	TEA	MeOH/Water	68	0.45	−53.19	−64.26
PA12	HDI	No Cat	MeOH/Water	64	0.42	−50.21	−54.95

[a]Method I: polymerization under conventional heating for 12 h at 120 °C. [b]Measured at a concentration of 0.5 g/dL in DMF at 25 °C. [c]Measured under conditions same as inherent viscosity.

method for reducing reaction time by several orders of magnitude and for increasing yields of product compared to conventional methods. The **IL**s are also suitable for microwave chemistry and it is expected that the high polarity of the **IL** makes it an efficient substrate for quick heating under microwave irradiation. We herein report an efficient, simplified and benign procedure for the preparation of **PA**s *via* direct polycondensation of diacid 7 with different aliphatic and aromatic diisocyanates 8–11 in molten TBAB as green media (Scheme 2). The significant advantages of using **IL** and microwave irradiation are to avoid the use of volatile and toxic organic solvents and drastically reduction of reaction time. The polymerization reaction has been carried out both by thermal heating (method I) as well as microwave irradiation (method II) and the results shown in Tables II and III. The optimization of the reaction conditions for methods I and II by varying reaction time, microwave power level, period of

heating and amount of **IL** was examined to provide polymers in high yields and inherent viscosities Table IV and Figure 3. The yields and inherent viscosities of the polymers obtained by microwave irradiation verses thermal heating are comparable with remarkable reduction in reaction time due to homogeneous heating throughout the reaction media by microwave irradiation as compared to convection currents in thermal heating. This methodology required only small amount of the **IL** to promote the polymerization. All of the **PA**s remained soluble in the reaction medium, thus permitting an increase their molecular weight and giving viscous solutions. Extended reaction time or higher power levels resulted in decreased yields and inherent viscosities for all **PA**s. This was due to decomposition of the reaction mixture. To avoid this trouble, the reactions were conducted with intermittent heating at a moderate power level with mixing. After the initial exposure for 60 s at 100% of power level (900 W) the reaction mixture

Table III. Reaction conditions for the polymerization of diacid 7 with different diisocyanates and some physical properties of **PA13-PA24** prepared by method II[a]

Polymer	Diisocyanate	Catalyst	Non-solvent	Yield (%)	η_{inh}[b] (dL/g)	$[\alpha]_D^{25}$[c]	$[\alpha]_{Hg}^{25}$[c]
PA13	MDI	TEA	MeOH/Water	78	0.38	−27.87	−29.17
PA14	MDI	No cat	MeOH/Water	69	0.31	−23.21	−28.74
PA15	MDI	Py	MeOH/Water	81	0.33	−26.18	−47.50
PA16	MDI	DBTDL	MeOH/Water	88	0.38	−40.00	−44.05
PA17	MDI	TBA	MeOH/Water	74	0.38	−22.11	−46.23
PA18	MDI	DABCO	MeOH/Water	72	0.35	−41.41	−51.36
PA19	IPDI	DBTDL	Water	84	0.26	−50.50	−59.33
PA20	IPDI	No Cat	Water	84	0.22	−54.15	−56.18
PA21	TDI	DBTDL	Water	89	0.39	−46.02	−54.85
PA22	TDI	No Cat	Water	81	0.29	−34.07	−48.28
PA23	HDI	DBTDL	MeOH/Water	79	0.31	−47.13	−50.41
PA24	HDI	No Cat	MeOH/Water	77	0.27	−31.74	−55.16

[a]**Method II**: The reaction mixture was irradiated in a microwave oven for 1 min then cooled and irradiated for 30 s again at 100% of its power level. [b]Measured at a concentration of 0.5 g/dL in DMF at 25 °C. [c]Measured under conditions same as inherent viscosity.

Table IV. Optimization of reaction conditions for the preparation of **PA**s using microwave irradiation (method II)

Polymer	Microwave power	Reaction time	Yield (%)	η_{inh}[a] (dL/g)	$[\alpha]_D^{25}$[b]	$[\alpha]_D^{25}$[b]
PA14	100	60 s[c]	—	—	—	—
PA14	100	70 s	48	0.19	−30.02	−32.12
PA14	100	80 s	63	0.23	−31.14	−37.49
PA14	100	90 s	71	0.27	−27.54	−27.89
PA14	100	100 s	70	0.27	−25.23	−30.33
PA14	100	110 s	66	0.28	−26.66	−29.87
PA14	100	120 s	63	0.28	−32.49	−34.14
PA14	100	130 s[c]	—	—	—	—
PA14	100	60 + 30 s	74	0.31	−23.08	−24.34
PA14	100	70 + 20 s	69	0.30	−23.14	−24.77
PA14	100	80 + 10 s	69	0.31	−23.21	−28.74
PA14	80	60 s[c]	—	—	—	—
PA14	80	70 s	46	0.19	−24.30	−27.47
PA14	80	80 s	57	0.21	−21.08	−25.49
PA14	80	90 s	62	0.22	−24.71	−24.97
PA14	80	100 s	64	0.22	−22.49	−22.81
PA14	80	110 s	65	0.22	−21.11	−23.97
PA14	70	60 s[c]	—	—	—	—
PA14	70	70 s	42	0.18	−26.41	−28.06
PA14	70	80 s	55	0.20	−24.85	−25.55
PA14	70	90 s	62	0.21	−24.70	−24.78
PA14	70	100 s	62	0.21	−23.74	−26.52
PA14	70	110 s	62	0.20	−22.14	−23.02

[a]Measured at a concentration of 0.5 g/dL in DMF at 25 °C. [b]Measured under conditions same as inherent viscosity. [c]Decomposition occurred at higher power or extended irradiation time.
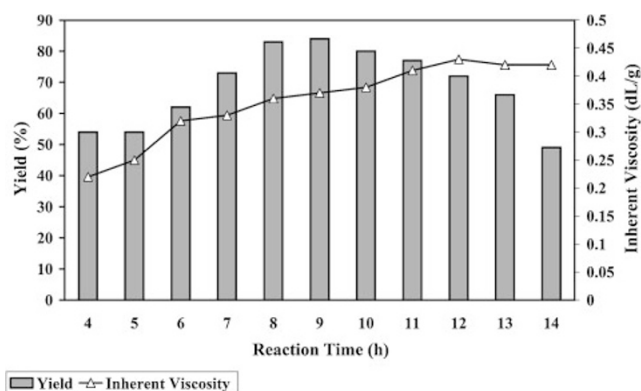

Figure 3. The effect of reaction time on the inherent viscosity and yield of **PA4** based on MDI by method I in the presence of DBTDL as a catalyst.

taken out, mixed for 2 min and then heated at the same power level for an additional 30 s. When the same experimental was conducted by conventional heating in the presence of TBAB it took 12 h for completion of polymerization reaction Tables II and III. On the other hand, a more homogeneous heating and outstanding rate quickening were observed under microwave irradiation. **PA**s made by different methods (Tables II and III) show different optical rotation and this is consistent for the all types of polymers made from different diisocyanates. These could be explained in terms of that optical rotation is highly dependent to the overall structure and regularity of the resulting polymer chains.

Polymer Characterization
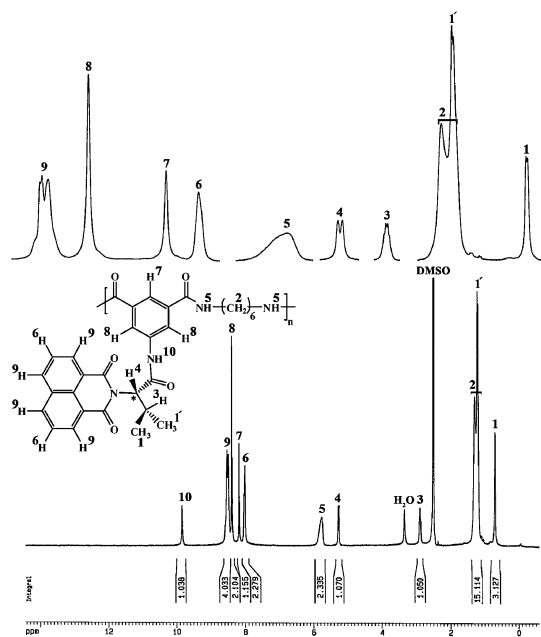
The structure of polymers was implemented by means of

Figure 4. ^{1}H NMR (500 MHz) spectrum of **PA12** in DMSO-d_6 at R.T.

Solubility Behavior of PAs

The solubility of **PA**s was tested quantitatively in various solvents. All of the **PA**s, are readily soluble in organic solvents such as DMF, DMAc, dimethyl sulfoxide, NMP, Py and in H_2SO_4 at room temperature and are insoluble in solvents such as chloroform, tetrahydrofuran, methylene chloride, cyclohexane, acetone and water. Some polymers were partially soluble in methanol and ethanol and precipitated in MeOH/water. The excellent solubility of these **PA**s is due to the presence of bulky side group which prevent the packing of the macromolecules through hydrogen bonds between amides groups in the chain and thus facilitate the diffusion of solvent molecules among the polymer chains.

Thermal Properties

The thermal stability of some **PA**s was investigated by TGA/DTG and DSC techniques under a nitrogen atmosphere. Figure 6 shows the TGA curves for **PA13**, **PA20**, **PA22** and **PA23**. Samples were heated up to 300 °C at the rate of 20 °C min^{-1} in N_2, quenched to −50 °C and return in order to obtain T_g. Thermal stability of the polymers was studied based on 5 and 10% weight loss (T_5, T_{10}) of the polymers and residue at 800 °C (char yield). Char yield can be used as criteria for evaluating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftyzer equation.[46] LOI = 17.5 + 0.4 CR where CR = char yield. All of the polymers had LOI values calculated based on their char yield at 800 °C was higher than 28. On the basis of LOI values, such macromolecules can be classified as self-extinguishing polymers. T_{10} (°C), Char Yield, T_g and LOI of these polymers are in the range of 361–440 °C, 45–47, 124–186 °C and 35–36, respectively. According to these data it is clear that polymers based on TDI and MDI have better thermal stability and higher LOI as compared to other **PA**s. It could be pertained to aromatic and rigid structure of diisocyanates compare to aliphatic, flexible structure of diisocyanates. The results are given in Table V and Figure 6.

elemental analysis, FT/IR and ^{1}H NMR (500 MHz) spectroscopy techniques. The elemental analysis results were in good agreement with calculated percentages for carbon, hydrogen and nitrogen contents in **PA**s repeating unit. The FT/IR spectra of polymers show peak around 3300 cm^{-1} for the N-H bond. Main absorption bands at 1770–1650 cm^{-1} range were attributed to the carbonyl groups. A strong band corresponding to C-N stretching can also be observed at 1340 cm^{-1}. The two absorption bands at 2900 and 2850 cm^{-1} are related to the corresponding C-H stretching vibration. The ^{1}H NMR spectra of polymers showed all peaks for aliphatic and aromatic protons which confirmed their structures. The resulting data are shown in Figures 4 and 5.
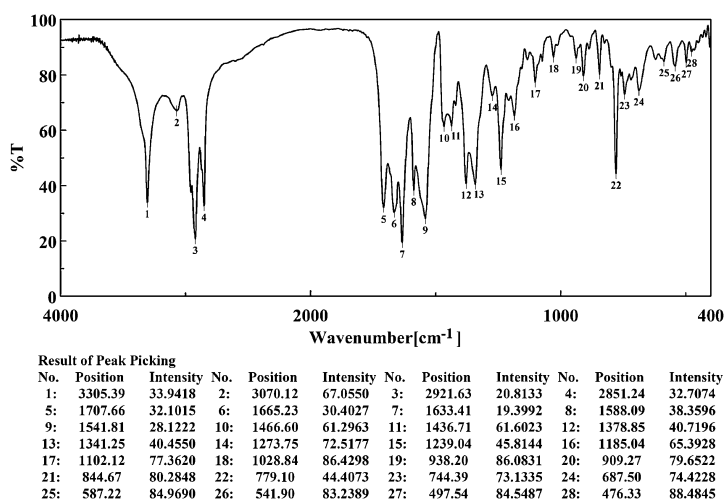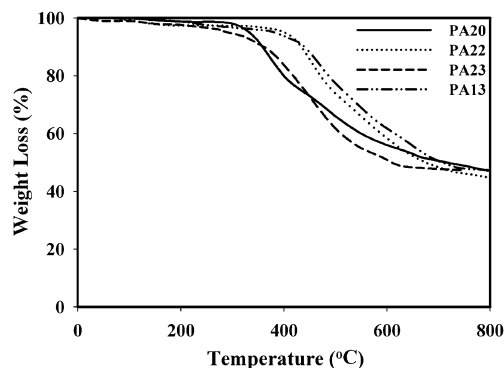

Result of Peak Picking

No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity	No.	Position	Intensity
1:	3305.39	33.9418	2:	3070.12	67.0550	3:	2921.63	20.8133	4:	2851.24	32.7074
5:	1707.66	32.1015	6:	1665.23	30.4027	7:	1633.41	19.3992	8:	1588.09	38.3596
9:	1541.81	28.1222	10:	1466.60	61.2963	11:	1436.71	61.6023	12:	1378.85	40.7196
13:	1341.25	40.4550	14:	1273.75	72.5177	15:	1239.04	45.8144	16:	1185.04	65.3928
17:	1102.12	77.3620	18:	1028.84	86.4298	19:	938.20	86.0831	20:	909.27	79.6522
21:	844.67	80.2848	22:	779.10	44.4073	23:	744.39	73.1335	24:	687.50	74.4228
25:	587.22	84.9690	26:	541.90	83.2389	27:	497.54	84.5487	28:	476.33	88.4845

Figure 5. FT/IR spectrum of **PA23**.

Figure 6. TGA thermograms of **PA13**, **PA20**, **PA22** and **PA23** under a nitrogen atmosphere at a heating rate of 10 °C/min.

Table V. Thermal properties of **PA13**, **PA20**, **PA22** and **PA23**

Polymer	T_5 (°C)[a]	T_{10} (°C)[b]	Char Yield (%)[c]	T_g (°C)[d]	DTG	LOI[e]
PA13	403	440	47	186	420	36.3
PA20	336	365	45	124	364	35.5
PA22	376	436	45	148	427	36.3
PA23	289	361	47	135	375	35.5

[a]Temperature at which 5% weight loss was recorded by TGA at a heating rate of 10 °C/min. in a nitrogen atmosphere. [b]Temperature at which 10% weight loss was recorded by TGA at a heating rate of 10 °C/min. in a nitrogen atmosphere. [c]Percentage weight of material left undecomposed after TGA analysis at a temperature of 800 °C in a nitrogen atmosphere. [d]Glass transition temperature was recorded at a heating rate of 20 °C/min in a nitrogen atmosphere. [e]Limiting oxygen index (LOI) was evaluated from char yield obtained at 800 °C.

Figure 7. UV-vis spectrum of monomer 7, **PA2**, **PA8** and **PA12**.
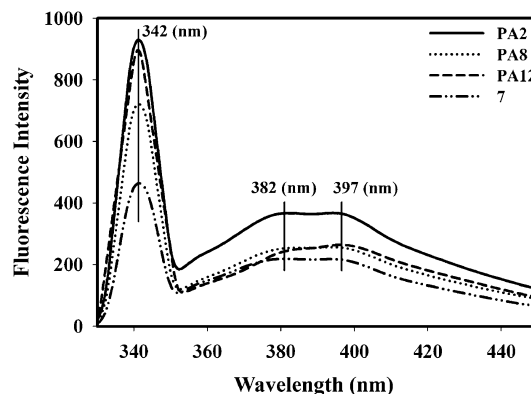
Figure 8. Fluorescence spectrum of monomer 7, **PA2**, **PA8** and **PA12**.

UV-vis Absorption and Fluorescence Characteristics

Polymers with fluorescent properties have been investigated in recent years. These polymers include chromophores in the backbone and polymers having chromophores as a pendant group. They are used as fluorescent labels and photoharvesters. Monomer 7 exhibited maximum UV-vis absorption at 264 and 335 nm in DMF solution because of the π–π^* transitions of the aromatic chromophore (naphthalene). In comparison of UV-vis absorption of the resulting polymers with a series of segmented **PA**s containing naphthalene show that the later polymers gave absorption at 264 and 335 nm in DMF solution.[37] The absorption and fluorescence spectra of 1.44×10^{-5} M, DMF solution of the monomer 7, **PA2**, **PA8** and **PA12** were shown in Figures 7 and 8. For example, in the case of the **PA2**; when it was excited at 265 nm, emission fluorescence wavelengths were observed at 342, 382 and 397 nm, respectively. The emission fluorescence pattern of these polymers was also compared with the **PA**s and poly(urea-urethane)s which gave similar pattern.[26,31,37] Because of these **PA**s have naphthalene functional group; they have potential to be used as photolabeling and photoresponsive materials. All of these compounds show almost similar UV-vis and fluorescence spectra pattern.

Kinetic Study

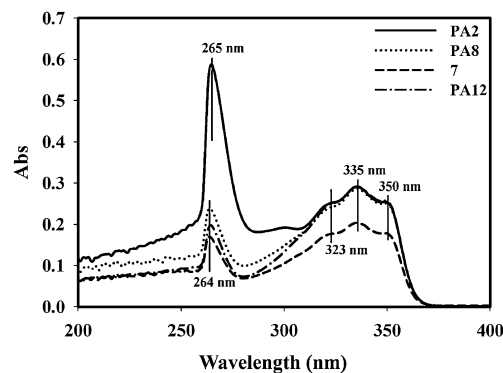There are usually some doubts about the accuracy of data obtained from the kinetic parameters which are estimated from the temperature integral. However, the most common application of these approximations is the determination of the activation energy and not the computation of the temperature integral. Thus in this paper, it is intended to perform a comparative study of the accuracy of such approximation to the temperature integral for the determination of the activation energy. In order to study the effect of different existing functional groups in the resulting **PA**s on their thermal stability, the thermal kinetic investigation was carried out using the Coats-Redfern (2) and Dharwadkar-Kharkhanawala (3) equations.[46–52] The results are listed in Table VI. The calculating of thermodynamic data applied on the decomposition peak in **PA13**, **PA20**, **PA22** and **PA23**.

$$\int_0^\alpha \frac{d\alpha}{(1-\alpha)^n} = \frac{A}{\varphi} \int_{T_1}^{T_2} \exp\left(-\frac{E^*}{RT}\right) dt \qquad (1)$$

For convenience of integration the lower limit T_1 is usually taken as zero. This equation upon integration gives the eq 2:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = -\frac{E^*}{RT} + \ln\left[\frac{AR}{\varphi E^*}\right] \qquad (2)$$

$$\ln\{1/(1-\alpha)\} = (E_a/RT_i^2)[100\theta/(T_f - T_i)] + C \qquad (3)$$

$$\Delta S = R \ln\left(\frac{Ah}{K_B T_S}\right) \qquad (4)$$

Table VI. Kinetic parameters for the degradation of **PA**s determined using the Coats-Redfern[1] and Dharwadkar-Kharkhanawala[2] equations

| Polymer[1]	Parameter					r
	E (kJ mol^{-1})	A (s^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	
PA13 (375–488)	54.43	163.19	−0.20	48.67	187.30	0.998
PA20 (310–415)	57.55	165.93	−0.20	52.29	178.92	0.999
PA22 (380–500)	110.43	42.33	−0.22	104.67	257.16	0.999
PA23 (310–430)	60.70	148.93	−0.20	55.31	184.94	0.998
Polymer[2]	Parameter					r
	E (kJ mol^{-1})	A (s^{-1})	ΔS (J mol^{-1} K^{-1})	ΔH (kJ mol^{-1})	ΔG (kJ mol^{-1})	
PA13 (375–488)	63.54	190.51	−0.20	57.77	196.40	0.997
PA20 (310–415)	58.07	156.77	−0.20	52.81	179.44	0.999
PA22 (380–500)	96.31	92.46	−0.21	90.55	236.11	0.997
PA23 (310–430)	63.76	172.98	−0.20	58.37	188.00	0.997
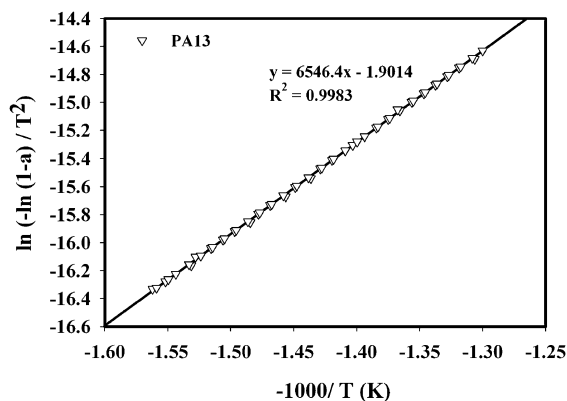
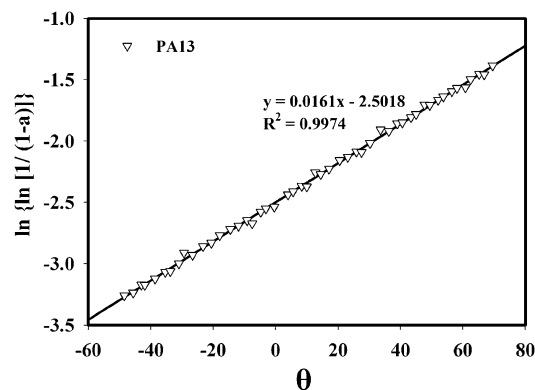**Figure 9.** Plot of $\ln[-\ln(1-\alpha)/T^2]$ against $-1000/T$ for **PA13**.

Figure 10. Plot of $\ln\{\ln[1/(1-\alpha)]\}$ against θ for **PA13**.

Where α and φ are the fraction of the sample decomposed at time t and the linear heating rate, respectively. R is the gas constant, E is the activation energy in kJ mol^{-1}, T_i = temperature of inflection of the reaction, T_f = temperature of completion of the reaction, $\theta = (T - T_s)$, difference between T_s and temperature under consideration, T_s = temperature at the point of inflection in T_g curve and C = constant. Plot of $\ln[-\ln(1-\alpha)/T^2]$ verses $-1/T$ and $\ln\{\ln[1/(1-\alpha)]\}$ against θ results in linear line with a slope of E_a/R and (E_a/RT_i^2) $[100/(T_f - T_i)]$ respectively (Figures 9 and 10). From the slope of these lines E, was calculated, and A (Arrhenius constant) can be deduced from the intercept. The enthalpy of activation, ΔH, and the free enthalpy of activation, ΔG, can be calculated *via* the equations; $\Delta H = E - RT_m$ and $\Delta G = \Delta H - T_m \Delta S$ accordingly, and are shown in Table VI. The positive values of ΔH indicate that the dissociation processes are endothermic in nature and enhanced with the rise of temperature. ΔG values for the dissociation constants are positive, thus dissociation processes are non-spontaneous. The overall activation energy and entropy for thermal decomposition of **PA**s based on TDI is 110.43 and -0.22 kJ mol^{-1} which is much higher than other **PA**s. This reveals that the more thermal stability and more ordered systems for this **PA**. One way to explain this behavior would be from the initial homolytic cleavage of ph-CH$_3$ bond which produces radical intermediate and therefore, provides a more stable cross-linked structure (Scheme 3).[52] The other way to explain this performance would be due to electron releasing

(+I effect) property of methyl group which activates the amide linkages and makes them highly activated for hydrogen bonding formation.

CONCLUSIONS

In summary, molten TBAB may act as a simple, cheap (compare to the room temperature **IL**s) and safe medium for polymerization reactions. The reported procedure for the polycondensation of new monomer 7 with various diisocyanates under green conditions demonstrates the potential of molten TBAB, a benign readily available **IL** as an efficient media and has much promise for further applications. Moreover, this methodology offers significant improvements with regard to yield of products, inherent viscosities, thermal stability, simplicity in operation, cost efficiency and green aspects avoiding toxic solvents. Moreover, the use of any organic solvent was not needed throughout the whole process of polymerization; in fact, organic solvent removal is of importance to minimize economic cost and environmental impact of chemical processes. A comparable result on the isolated yields and inherent viscosities was obtained by microwave irradiation verses thermal heating with remarkable reduction in reaction time. The incorporation of naphthalimide and S-valine groups, through an amide unit into **PA**s backbone gave polymers with remarkable solubility in common organic solvents. Because of the existence of amino acids in the
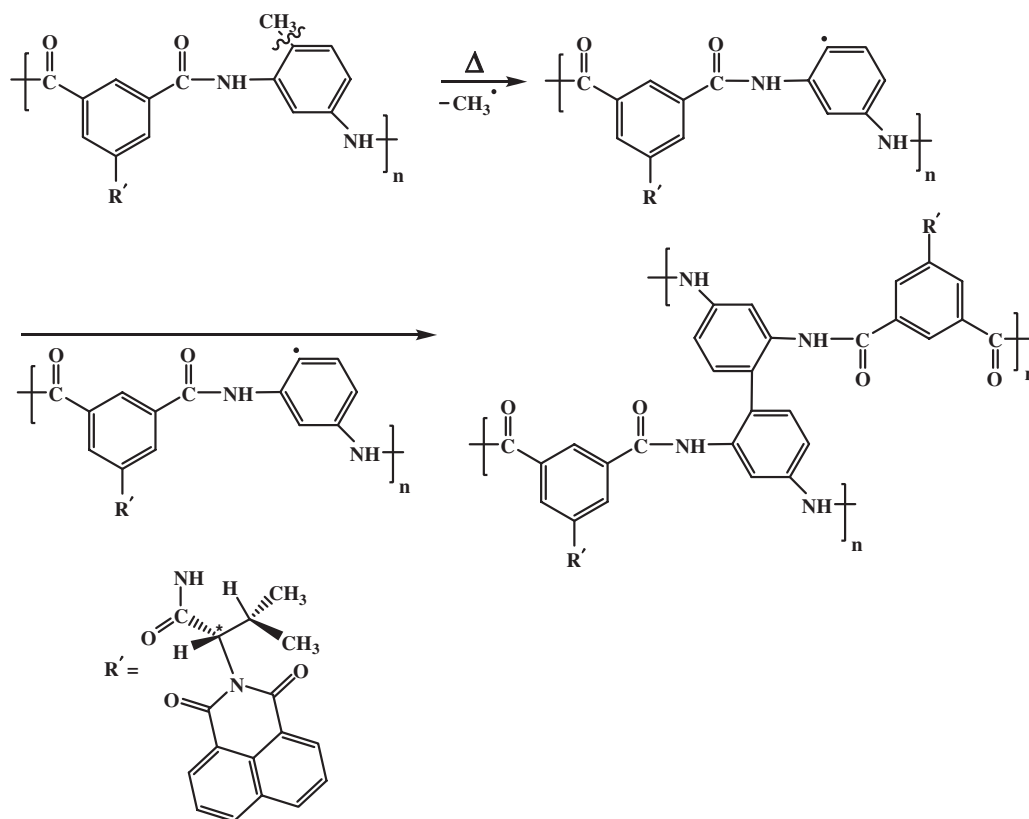
Scheme 3.

polymer pendent group these polymers are expected to be biodegradable and are therefore classified under environmentally friendly polymers. The thermal degradation of **PA**s was analyzed using Coats-Redfern and Dharwadkar-Kharkhanawala methods. The corresponding kinetic parameters were calculated to well interpret the relationship between the composition of **PA**s and their stability. Furthermore, it is very interesting to mention that in this study the data obtained by two above different methods will lead us to predict the reaction mechanism of thermal degradation of the resulting **PA**s.

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