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Fast and Eco-friendly Synthesis of Novel Soluble Thermally Stable Poly(amide-imide)s Modified with Siloxane Linkage with Reduced Dielectric Constant under Microwave Irradiation in TBAB, TBPB and MeBuImCl via Isocyanate Method

Fatemeh Rafiemanzelat,[1] Seyyed Mahmood Khoshfetrat,[1] Majid Kolahdoozan[2]
[1]Department of Chemistry, Organic Polymer Chemistry Research Laboratory, University of Isfahan, Isfahan 81746-73441, Iran
[2]Department of Chemistry, Organic Polymer Chemistry Research Laboratory, Islamic Azad University, Shahreza Branch, Shahreza, Isfahan, 311-86145, I.R. Iran

Correspondence to: F. Rafiemanzelat (E-mail: frafiemanzelat@chem.ui.ac.ir)

ABSTRACT: A new series of poly(amide-imide)s (PAI) modified with a siloxane linkage was synthesized under microwave radiation in ionic liquids and organic salts via the isocyanate method. The polymerization reactions of a novel siloxanic diacid monomer with 4,4′-methylene-bis(4-phenylisocyanate) MDI were studied in ammonium, phosphonium, and imidazolium-type organic salts. These poly(amide-imide-siloxane)s (PAI-Si)s were obtained with high yields and good inherent viscosities ranging from 0.30 to 0.55 dL/g. The normally high softening temperatures and poor solubility of PAIs in organic solvents were improved via the incorporation of the flexible siloxane segments into the polymer backbone. The PAI-Sis showed glass transition temperatures around 100°C and their 10% mass loss was about 300°C. They have a char yield in the range of 30–40% at 800°C. Calculated limiting oxygen index values of the polymers were about 30; therefore, they can be considered as self-extinguishing. The dielectric constants of these silane-containing PAIs (2.5) are lower than common siloxane-free polyimides (~ 3). Their good thermal stability, enhanced solubility, and low dielectric constants suggest they may function as electrical insulators. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: poly(amide-imide-siloxane); microwave irradiation; thermally stable; process-ability; ionic liquids

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INTRODUCTION

Many chemical processes involve volatile organic solvents (VOSs) that evaporate into the atmosphere with detrimental effects on human health and the environment. Thus, the use of reaction media like water, supercritical fluids or ionic liquids (IL)s, and so forth, has received a lot of attention as an environmental friendly alternative to organic solvents. Thus, researchers are trying to redesign chemical processes to reduce or eliminate losses of VOSs.[1–8] For example, successful application of ILs as well as nonvolatile organic salts (NVOSs) in synthesis of different condensation polymers has been reported.[9–20]

Microwave irradiation is utilized in many private households and industrial applications for heating and drying materials. It offers a number of advantages over conventional heating. It shows a uniform and highly specific heating of the reaction fluids due to direct and rapid heating with the material selectivity.[21–25] A large number of reactions, including polymerization reactions were studied under microwave heating. It reduces reaction times, increase product yields, produce narrow molar mass distributions for polymers, and enhance product purities and selectivity by reducing unwanted side reactions.[24–36] Thus, combining the advantages associated with the green solvent aspect of NVOSs with microwave heating can afford a fast and eco-friendly technique for the production of polymers.[37–40]

Polyimides are one of the most important classes of high performance polymers, because of their outstanding thermal stability, chemical resistant, good mechanical strength, low coefficient of friction, good electrical properties, and low dielectric constant.[41–43] Polyimides have found a wide range of applications in the aerospace, automobile, and microelectronics industries in severe environments due to their advantageous properties.[41–46] However, their applications may be rather limited due to their high softening or melting temperatures and poor solubility in most organic solvents. Thus, polyimide's structures are modified by introduction of flexible linkages, or synthesizing copolymers with improved process-ability such as poly(amide-imide)s (PAI)s.[47,48] In additions incorporation of low-polarizing siloxane units into the polyimide backbones improves their solubility and decreases their dielectric constant while maintaining their high performance properties. The siloxane imparts a number of additional benefits to the copolymer system, including reduced water absorption, high gas permeability, modified surface properties, good resistance to aggressive oxygen, good adhesive properties, and improved flame resistance.[41,45,49–53]

Copolymers of PAIs usually are synthesized from various monomers containing anhydride, carboxylic acid, diacyl chlorides and diamines by condensation. The use of dicarboxylic acids in direct polycondensation instead of their more reactive but more toxic derivatives, such as acid chlorides, is one of the important basics for the synthesis of such polymers. Conversely, direct polyamidation methods based on the reaction of diacids and diamines use VOSs and many dehydrating agents such as triphenyl phosphate, *N*-methyl-2-pyrrolidinone (NMP), pyridine (Py), *N*,*N*-dimethylformamide (DMF), and so forth. which make the methods environmentally unfriendly. Here, we used isocyanate method for polyamidation reaction that can omit all of the aforementioned compounds. The conventional method used in poly(imide-siloxane) synthesis is the reaction of amino-terminated dimethylsiloxane oligomers with dianhydrides and additional diamines. Usually, subambient temperatures and aprotic dipolar solvents are used. The resultant polyamic acid solution can be heated to achieve imidization and solvent evaporation, the same as procedure used to prepare conventional polyimides. Here, we used isocyanate method for polyamidation reaction between diisocyanates and a new siloxanic diacid having a preformed imide ring, to prepare novel copoly(amide-imide-siloxane). Thus, this method can omit all of the aforementioned solvents, reaction steps, dehydrating agents, and organic compounds. In additions as a part of our program to avoid VOSs and toxic catalysts in reactions, we have investigated the use of NVOSs and ILs including tetra-butylammonium bromide (TBAB), tetra-butylphosphonium bromide (TBPB), and 1-buthyl-3-methyl imidazolium chloride (BuMeImCl) as reusable reaction media for a fast, convenient, cost effective, and environmentally benign method under microwave irradiation.

EXPERIMENTAL

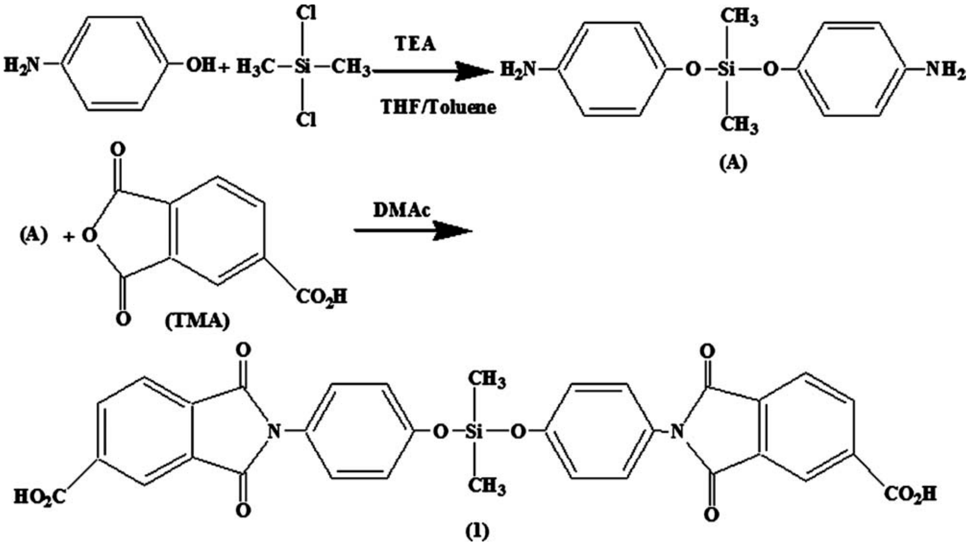
Materials and Equipments

4,4′-Methylene-bis(4-phenylisocyanate) (MDI) a high purity Aldrich product, was used as received. TBAB, TBPB, and BuMeImCl, were purchased from Merck and were used without further purification. *N*-Methyl pyrrolidone (NMP) (Merck), *N*,*N*-dimethylacetamide (DMAc) (Merck), pyridine (Py) (Merck), and triethylamine (TEA) (Merck) were distilled under reduced pressure over BaO (Merck). Tetrahydrofurane (Merck) and toluene were dried over Na and distilled. Trimellitic acid anhydride (TMA) (Merck) and dibutyltin dilaurate (DBTDL) (Merck) were used as received.

^{1}H-NMR (400 MHz) spectra were recorded on a Varian inova-400 in dimethyl sulfoxide (DMSO)-d_6 at room temperature (RT) by the Research Institute of Polymer and Petrochemical of Iran. Multiplicities of proton resonance were designated as singlet (s), and doublet (d). FTIR spectra were recorded on a shimadzu FTIR 8000 series spectrophotometer by central laboratory of Shiraz University. Spectra of solids were performed using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), strong (s), sharp (sh), and broad (br). Inherent viscosities were measured at RT by a standard procedure using a Cannon-Fensk Routine Viscometer (Germany). Thermal gravimetric analysis (TGA) data for polymers were taken on a Mettler-Toledo TG-50 Thermal Analyzer under N_2 atmosphere at heating rate of 20°C/min. Differential scanning calorimetery (DSC) data for polymers were recorded on a DSC-30/S instrument under N_2 atmosphere. Glass or melting transition temperatures (T_g/T_m) were read at the middle of the transition in the heat capacity taken from heating DSC traces. A heating rate of 10°C/min was applied to all samples. Wide angle X-ray diffraction (WAXS) measurements were performed with a Bruker, D8advance XRD Diffractometer using a graphite monochromatized Cu Ka radiation (40 kV; 40 mA). Refractive index of polymer thin films was measured with a Metricon Prism Coupler PC-2000 (Pennington, NJ). The molecular weights (M_w and M_n) were determined by gel permeation chromatography (GPC). It was performed on a Waters 150C instrument using Styragel columns and a differential refractometer detector. The molecular weight calibration was performed using polystyrene standards. Calibration and measurements were made at a flow rate of 1 mL/min, and DMF was used as solvent. The apparatus used for the polycondensation was a Samsung microwave oven (2450 MHz, 900 W). All of the polymerization reactions were performed in a hood with strong ventilation.

Synthesis of Siloxanic Diacid (1)

A typical procedure for the synthesis of (1) was as follows[41]: into a three-necked flask, mixture of 4-aminophenol (2.2 g, 0.02 mol), TEA (2.2 g, 0.02 mol), 25 mL of THF, and 5 mL of toluene were introduced. Then, a solution of dichlorodimethylsilane (1.3 g, 0.01 mol) in 10 mL THF was added into the mixture drop wise over a period of 45 min at 75°C. The reaction mixture was refluxed for 3 days. Formed salt was removed from the mixture by filtration and the filtrate was concentrated by a rotary evaporator. Then, it was dissolved in ether and the precipitated salt was isolated by filtration. The crude product was crystallized from ether at 0°C to yield brown-yellow crystals and dried under reduced pressure at 60°C for 48 h. The yield of reaction was 85% (Product A). Then into a 50-mL, round-bottomed flask equipped with a magnetic stirrer, nitrogen gas inlet tube, reflux condenser and a calcium chloride drying tube the resulting product A (2.58 g, 0.01 mol) and TMA (3.8 g, 0.02 mol) were dissolved in 15 mL dried DMAc. The mixture was stirred at RT for 24 h. Then, the temperature was raised and the solution was refluxed for 12 h. The solution was concentrated by a rotary evaporator. Crude diacid product was precipitated by pouring the flask content into mixture of water/HCl 37% (1/5), it was then filtered, washed with hot water (50°C), and dried overnight at 50°C. Then, it was recrystalized from hot methanol to give diacid (1) in 80% yield. **^{1}H-NMR** (DMSO-d_6, TMS, 400 MHz, δ ppm) of diacid (1): 0.16 (s, 6H,



Scheme 1. Synthesis of siloxanic diacid monomer (1).

$SiCH_3$), 6.80 (d, $j = 7.4$ Hz, 4H, Ar), 7.40 (d, $j = 7.4$ Hz, 4H, Ar), 8.29 (d, $j = 6.9$ Hz, 2H, Ar), 8.37 (d, $j = 7$ Hz, 2H, Ar), 8.8 (br, 2H, Ar), 11.4 (s, br, 2H, COOH).

Polymer Synthesis

Polymerization Reaction of Siloxanic Diacid (1) with MDI (2) in TBAB Under Microwave Irradiation. The PAIs were prepared by the following general procedure, as an example for the preparation of PAI2: into a porcelain dish was placed 0.050 g (7.32×10^{-5} mol) of diacid (1) and 0.34 g (1.00×10^{-3} mol) of TBAB. After the mixture was completely ground, MDI 0.018 g (7.10×10^{-5} mol) was added and grinding was continued. The reaction mixture was irradiated in a microwave oven for 8 min at 100% of its power. The resulting product was isolated by the addition of 10 mL of methanol. It was then filtered off and dried at 80°C for 10 h in vacuum; this yielded 0.057 g (95%) of yellow PAI2. **FTIR (KBr):** 3320 (w, br), 3050 (w), 3010 (w), 2980 (w), 1670 (w), 1720 (s), 1660 (m), 1610 (m), 1570 (w), 1510 (s), 1430 (w), 1400 (m), 1290 (w), 1250 (w), 1210 (s), 1180 (m), 1110 (w), 1010 (w), 960 (w), 920 (w), 830 (w), 800 (w), 770 (w), 720 (m), 700 (w), 640 (w), 610 (w), 560 (w), 510 (w), 450 (w), and 420 (w)

The above polymerization method was repeated in the presence of Py, TEA, or DBTDL, respectively.

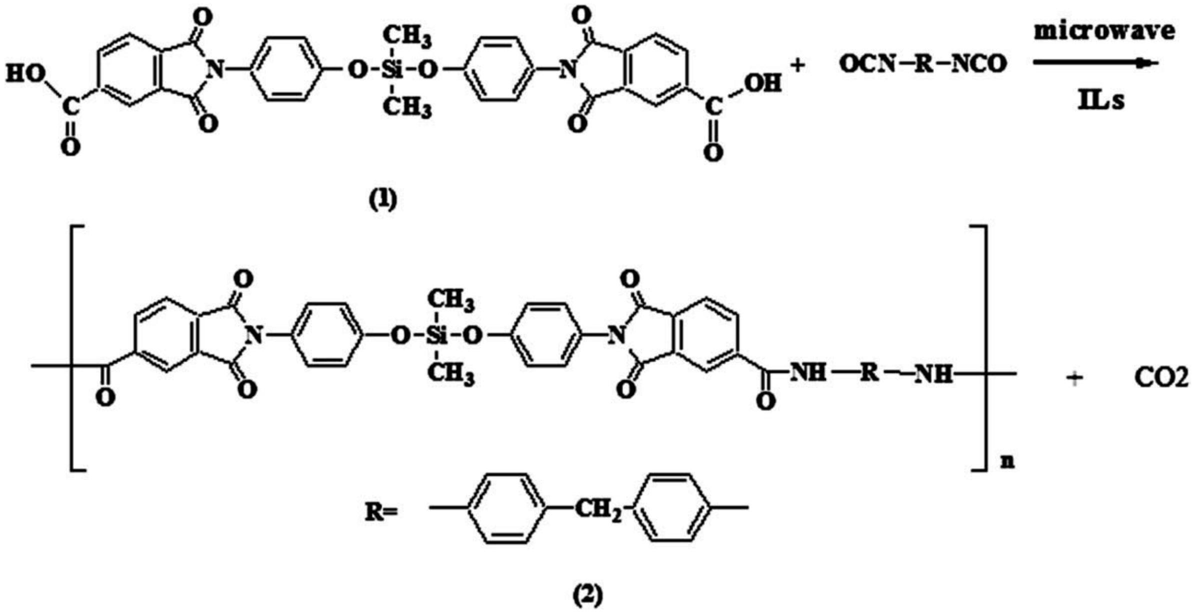
Polymerization Reaction of Siloxanic Diacid (1) with MDI (2) in Imidazolium-Based ILs Under Microwave Irradiation. As an example, preparation of PAI6 in $BuMeImCl^-$ was as follows: into a porcelain dish was placed 0.050 g (7.32×10^{-5} mol) of diacid (1) and 0.136 g (7.78×10^{-4} mol) of $BuMeImCl^-$. After the mixture was completely ground, MDI 0.018 g (7.10×10^{-5} mol) was added and grinding was continued. The reaction mixture was irradiated in a microwave oven for 8 min at 70% of its power. The resulting product was isolated by the addition of 10 mL of a mixture of methanol/water (50/50). It was then filtered off and dried at 80°C for 10 h in vacuum; this yielded 0.05 g (82%) of yellow PAI6. **FTIR (KBr):** 3319 (w, br), 3038 (w), 1778 (w), 1709 (s,s), 1600 (m, s), 1517 (s, sh), 1456 (m), 1390 (s, sh), 1212 (m), 1096 (s, m), 927 (w), 834 (m), 728 (s, sh), 690 (w). **^{1}H-NMR (DMSO-d_6)**, TMS, 400 MHz, δ ppm) of PAI6: 1.14 (s, 6H, $SiCH_3$), 3.76 (s, 2H, CH_2), 6.85(d, $j = 7.4$ Hz, 4H, Ar), 7.06 (d, $j = 5.2$ Hz, 4H, Ar), 7.19 (d, $j = 7.4$ Hz, 4H, Ar), 7.29 (d, $j = 5.2$ Hz, 4H, Ar), 8.01(d, $j = 6.9$ Hz, 2H, Ar), 8.25 (s, 2H, Ar), 8.37 (d, $j = 7$ Hz, 2H, Ar), 9.7 (s, 2H, NH).

Polymerization Reaction of Siloxanic Diacid (1) with MDI (2) in TBPB Under Microwave Irradiation. The PAIs were prepared by the following general procedure, as an example for the preparation of PAI10: into a porcelain dish was placed 0.050 g (7.32×10^{-5} mol) of diacid (1) and TBPB (0.136 g, 4.00×10^{-4} mol). After the mixture was completely ground, MDI (0.018g, 7.10×10^{-5} mol) was added and grinding was continued. The reaction mixture was irradiated in a microwave oven for 8 min at 100% of its power. The resulting product was isolated by the addition of 10 mL of methanol/water (50/50). It was then filtered off and dried at 80°C for 10 h in vacuum; this yielded 0.053 g (89%) of yellow PAI10. **FTIR (KBr)**: 3340 (m, br), 3020 (w), 2920 (w) 1710 (s), 1670 (m), 1590 (w), 1530 (m), 1523 (s), 1430 (w), 1380 (m), 1250 (w), 1230 (w), 1200 (w), 1150 (w), 1100 (w), 1050 (w), 900 (w), 890 (w), 850 (w), 870 (w), 750 (w), 720 (w), 700 (w), 610 (w), and 600 (w)

RESULTS AND DISCUSSION

Polymerization Reaction

The aim of this work is the synthesis of new thermally stable as well as soluble PAIs. These novel PAIs is going to be prepared by the reaction of a new diacid monomer with MDI through isocyanate route. Thermal and solubility modification of these PAIs is performed by the introduction of siloxane flexible linkage. This structural feature is expected to enhance solubility and decrease T_g softening point of polymers together with maintaining their thermal stability. The effect of low-polarizing siloxane units into the polymers' backbone on their solubility and dielectric constant is also studied. Thus in this research a siloxanic diacid monomer, (1), containing a preformed imide ring was



Scheme 2. Preparation of PAIs-Si via polycondensation reaction of monomer (1) with MDI (2) in different ILs/NVOS under microwave irradiation.

successfully synthesized in two steps and used for the preparation of a series of novel thermally stable and organo soluble PAIs. Chemical structure and purity of (1) were confirmed by TLC, FTIR, and ^{1}H-NMR techniques (Scheme 1).

The polymerization reactions of monomer (1) with MDI diisocyanate were performed under microwave irradiation in different types of NVOSs and ILs and compared with conventional heating techniques (Scheme 2).

There is a tendency in speeding up synthetic transformations by using NVOSs and ILs as reaction media, in microwave heated reactions. It was shown that NVOSs and ILs with the assistance of microwave irradiation can yield fast, novel, efficient, and green synthetic techniques. Reactions of MDI with (1) in NVOSs and ILs were also performed by thermal heating in oil bath and compared with microwave irradiation techniques. The results obtained under thermal heating were not acceptable. Yields and inherent viscosities were too low after extended reaction time.

One of the key objectives of our approach was to determine the optimal set of reaction conditions that can grant polymers with good yields and inherent viscosities. Thus for each type of NVOSs and ILs, for example, ammonium, imidazolium, and phosphonium types, the optimum conditions under microwave irradiation, after several experimentations were found as follows: for TBAB reaction time 2 + 2 + 2 + 2 min, power level 100%, ratio of salt to monomers 5/1 (w/w) (Table I), for BuMeImCl reaction time 2 + 2 + 2 + 2 min, power level 70%, ratio of IL to monomers 2/1 (w/w) (Table II), and for TBPB reaction time 2 + 2 + 2 + 2 min, power level 100%, ratio of salt to monomers 2/1 (w/w) (Table III). The effects of varying the quantity of NVOSs or ILs were also studied. It was found that the aforementioned salts/monomers ratios were the best amount under microwave irradiation. Higher or lower amounts of NVOSs or ILs resulted in decreased yields and inherent viscosities due to the decomposition of the reaction mixture.

It is interesting to mention that, polymerization reactions of (1) with MDI in TBAB, BuMeImCl, and TBPB under aforementioned optimized reaction conditions were studied with or without DBTDL, Py, or TEA as reaction catalysts, respectively. For example, Table IV represents resulting data in TBAB. The results were relatively similar in the presence of DBTDL, Py, and TEA. To some extent, better viscosity, and yield were obtained in the

Table I. Optimizing Reaction Time for the Polymerization of (1) with MDI (2) in TBAB Under Microwave Irradiation at 100% of its Power

Polymer	Reaction time (min)	Yield (%)	η_{inh}(dL g^{-1})^a
PAI1	7.30	92	0.38
PAI2	8	95	0.45
PAI3	9	91	0.43
PAI4	11	70	0.39

[a] Inherent viscosity of polymer, measured at a concentration of 0.5 g/dL in DMF at 25°C.

Table II. Optimizing Reaction Time for the Polymerization of (1) with MDI (2) in BuMeImCl$^-$ Under Microwave Irradiation at 70% of its Power

Polymer	Reaction time (min)	Yield (%)	η_{inh} (dL g^{-1})^a
PAI5	7 .30	76	0.50
PAI6	8	82	0.50
PAI7	9	80	0.44
PAI8	10	70	0.41

[a] Inherent viscosity of polymer, measured at a concentration of 0.5 g/dL in DMF at 25°C

Table III. Optimizing Reaction Time for the Polymerization of (1) with MDI (2) in TBPB Under Microwave Irradiation at 70% of its Power

Polymer	Reaction time (min)	Yield (%)	η_{inh}(dL g^{-1})^a
PAI 9	7	78	0.43
PAI 10	8	90	0.52
PAI 11	9+30 sec	79	0.47

[a] Inherent viscosity of polymer, measured at a concentration of 0.5 g/dL in DMF at 25°C.

Table IV. Optimizing Reaction Conditions for the Polymerization of (1) with MDI (2) Under Microwave Irradiation at 100% of its Power and 8 min Irradiation in TBAB; Effect of Using Catalyst

Polymer	Catalyst	Yield (%)	η_{inh}(dL g^{-1})^a
PAI12	No	95	0.45
PAI13	Py	86	030
PAI14	TEA	75	0.39
PAI15	DBTDL	88	0.39

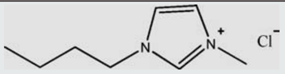
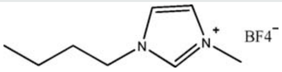
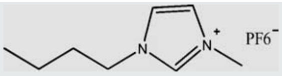
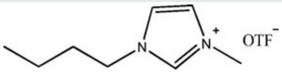
[a] Inherent viscosity of polymer, measured at a concentration of 0.5 g/dL in DMF at 25°C.

absence of any catalysts, indicating that, the catalyst was not necessary in this process.

Aforementioned methods were compared with the polymerization reactions in conventional solvent, NMP, under microwave irradiation in the presence or absence of above catalysts. Polymers were obtained with high yields and good inherent viscosities ranging from 0.54 to 0.82 dL/g. In the case of using NMP optimized reaction conditions were as follows: reaction time 2 + 2 + 1 min, power level 100%, ratio of solvent to monomers 2.5/1 (v/w) in the presence of DBTDL as catalyst. However; in this process NMP has been used as reaction solvent which is volatile, and will cause a change in the concentration of reaction mixture during polymerization reaction, consequently leading broader polydispersity (PD). NMP decomposed during irradiation and is not reusable. Conversely, catalyst was required to be used in this method. NMP is a VOS and insecure for environment. In the case of polymerization reactions in NVOSs, it can be said that TBAB, BuMeImCl and TBPB can be used as nonvolatile reaction media which are green, and safe, and DBTDL was eliminated which also decreases the cost and pollution. They act as effective solvents and catalysts to mediate clean polymerization reactions. Thus, polymerization reactions can be conducted without additional catalyst and conventional solvent. Conversely, our study shows that TBAB and TBPB are reusable up to more than four times which reduces the cost and pollution as well.

The optimized reaction conditions established for the polymerization reaction of (1) and MDI in TBAB, BuMeImCl, and TBPB, respectively, were used for studying the reaction of (1) and MDI in other ammonium, imidazoliun, and phosphonium type salts. In the case of imidazolium types ILs bearing different anions including BF_4^-, $CF_3SO_3^-$, Cl^-, and PF_6^- the best inherent viscosity and yield were obtained in BuMeImCl (Table V). In the case of ammonium types organic salts including TBAB, tetrapropylammonium bromide, benzyl tributyl ammonium chloride, hexadecyltrimethylammonium bromide, and *n*-dodecylpyridinium chloride our studies showed that polymers were formed only in the presence of TBAB. In the case of phosphonium types salts including TBPB, hexadecyltributhyl phosphonium bromide (HDTBPB), and tetraoctyl phosphonium bromde (TOPB) our detailed studies showed that inherent viscosities and yields obtained in HDTBPB and TOPB were rather too low.

Table V. The Influence of Different Imidazolium ILs on Yields and Viscosities of PAI-Sis Prepared Under Optimized Reaction Condition Obtained in ($BuMeImCl^-$) Under Microwave Irradiation

Polymer	IL structure	IL	Yield (%)	η_{inh} (dL g^{-1})^a
PAI16		($BuMeImCl^-$)	82	0.55
PAI17		($BuMeImBF_4^-$)	81	0.36
PAI18		($C_8H_{15}N_2PF_6^-$)	71	0.43
PAI19		($BuMeImOtf^-$)	76	0.40

[a] Inherent viscosity of polymer, measured at a concentration of 0.5 g/dL in DMF at 25°C.

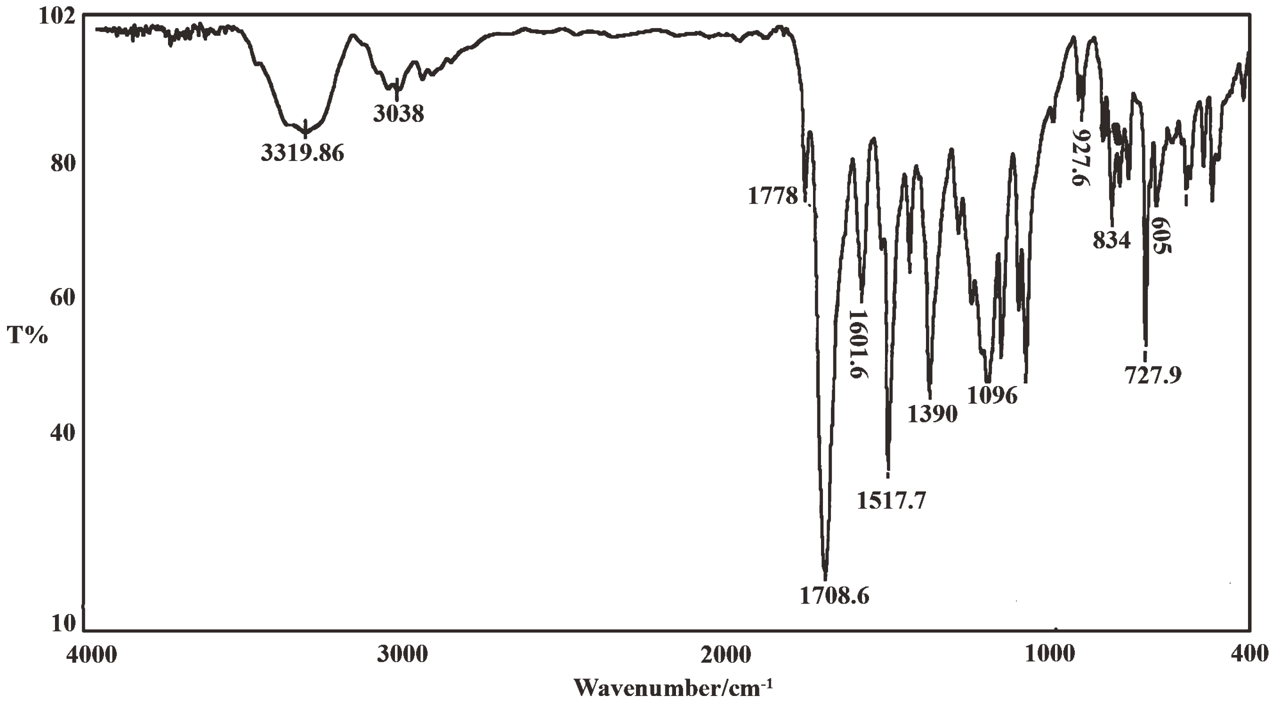


Figure 1. FTIR (KBr) spectrum of PAI5.

Estimation of the molecular weight of PAI16 (η_{inh} = 0.55 dL/g) was achieved using GPC method in DMF over polystyrene standard. Its M_n, M_w, and PD were 45,800, 70,200, and 1.53, respectively. To compare the effect of conventional solvent with IL on M_n, M_w, and PD of polymers, molecular weight of poly(amide-imide-siloxane) (PAI-Si) prepared in NMP (η_{inh} = 0.8 dL/g) (PAI_{NMP}) was obtained using GPC method in DMF over polystyrene standard as well. Its M_n, M_w, and PD were 44,054, 77,976, and 1.77, respectively, which shows broader PD than that of PAI16.

Polymer Characterization

The resulting polymers were characterized by FTIR and ^{1}H-NMR spectroscopy.

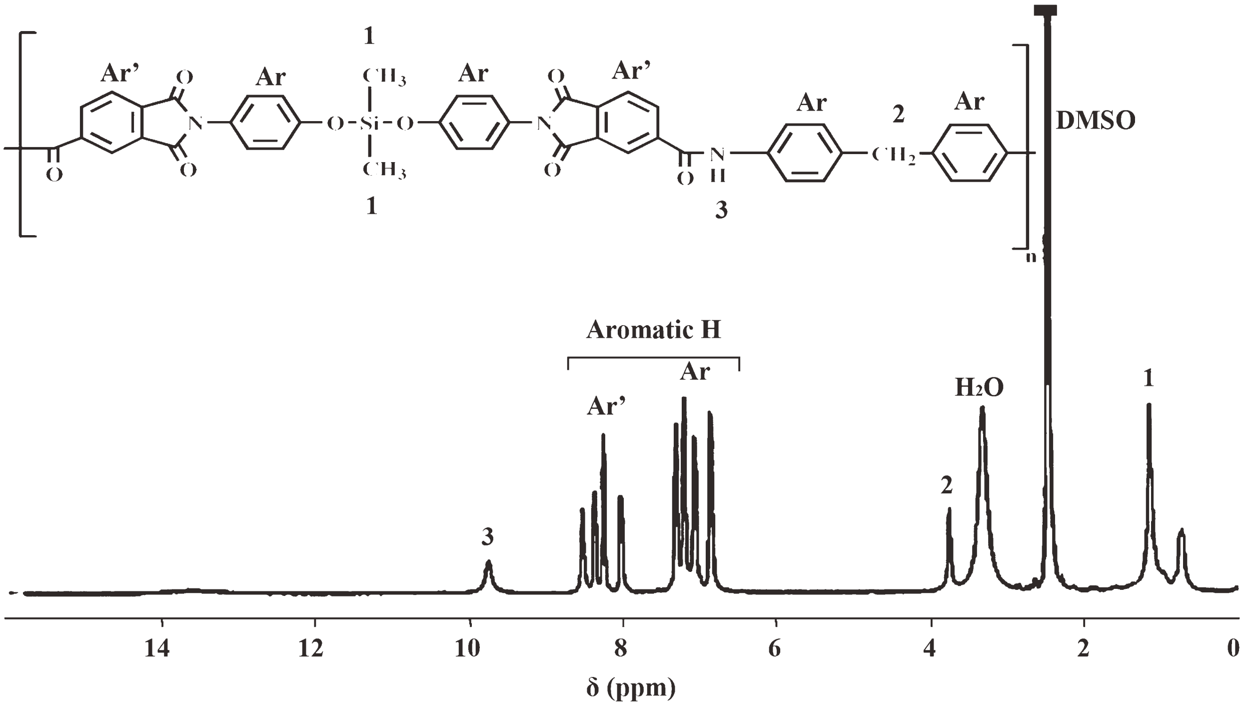


Figure 2. ^{1}H-NMR (400 MHz) spectra of PAI6, in DMSO-d_6 at RT.

Table VI. Thermal Stability and Thermal Behaviors Data of PAI-Sis by TGA and DSC

Polymer	T5 (°C)[a]	T10 (°C)[b]	Char yield (%)[c]	T1 (°C)[d]	T2 (°C)[e]
PAI12	240	250	32	96	269 (dec)[f]
PAI5	250	268	39	105	271 (dec)[f]
PAI10	253	279	40	108	269 (dec)[f]
PAI_{NMP}[g]	270	290	40	96	300 (dec)[f]

[a] Temperature at which 5% weight loss was recorded by TGA at heating rate of 20°C/min in N_2, [b] Temperature at which 10% weight loss was recorded by TGA at heating rate of 20°C/min in N_2, [c] Percentage of weight residue at 700°C recorded by TGA at heating rate of 20°C/min in N_2, [d] Glass transition temperature of polymer was read at the middle of the transition taken from the heating DSC traces at heating rate of 10°C/min in N_2, [e] Glass or melting transition temperature of rigid segments of polymer was read at the middle of the transition taken from the heating DSC traces at heating rate of 10°C/min in N_2, [f] Thermal degradation in accordance with T10 in TGA thermogram, [g] PAI prepared in conventional organic solvent (NMP).

The FTIR spectra of PAIs-Si showed peaks, which confirm their chemical structures. As an example, the FTIR spectrum of PAI5 showed the characteristics absorptions of amide and imide groups around 3150, 1780, 1710, and 1514 cm^{-1}, peculiar to NH stretching and carbonyl stretching of imide and amide groups, respectively. Absorption bands of $SiCH_3$, Si—O—Si, $Si(CH_3)_2$ occurred around at 1200, 1100, and 800 cm^{-1}, respectively. All PAIs-Si exhibited absorption bands around 1300–1400, and 720 cm^{-1} due to the presence of the heterocyclic imide group in the polymer backbone (Figure 1).

The ^{1}H-NMR spectrum of PAI6 showed peaks that confirms its chemical structure. It shows peaks for Si—CH_3 (1) in the region of 1.14 ppm. Peak in the region of 3.76 ppm are related to CH_2 (2). The aromatic protons appeared in the region of 6.38–8.52 ppm, where peaks in the region of 8.01–8.37 ppm are related to TMA aromatic ring moiety. A broad peak in the region of 9.75 ppm is assigned for NH of amide groups (Figure 2).

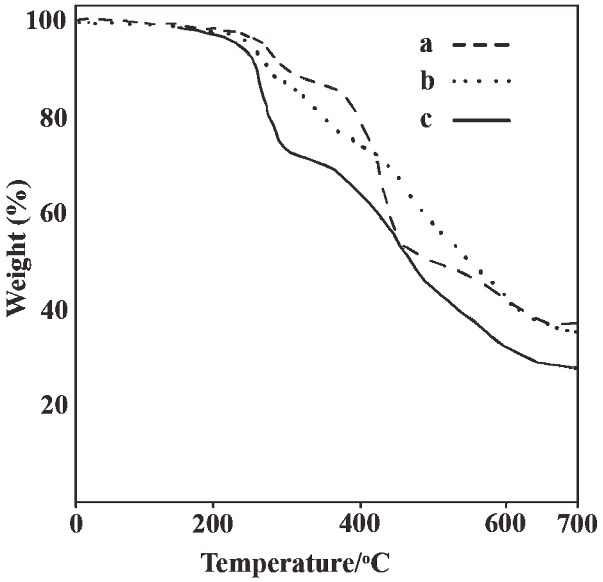


Figure 3. TGA thermograms of PAI10 (a), PAI5 (b), and PAI12 (c) with a heating rate of 20°C/min in N_2.

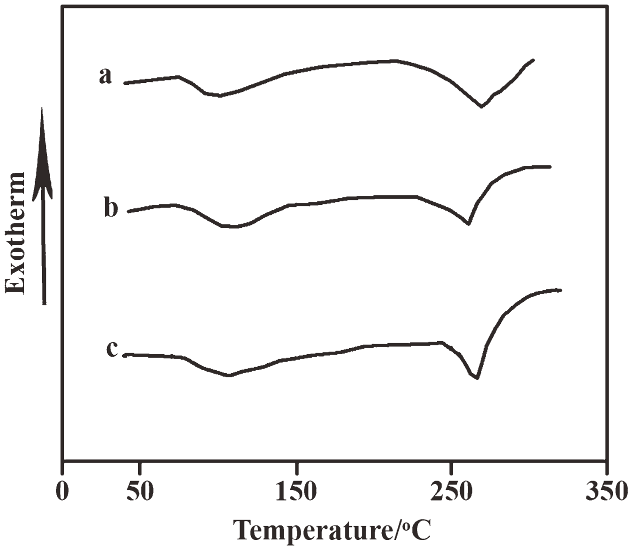


Figure 4. DSC traces of PAI2 (a), PAI5 (b), and PAI10 (c) at heating rate of 10°C/min under N_2 atmosphere. Center of the region was considered for transition observed by DSC.

Solubility Properties of Polymers

All polymers are soluble in aprotic polar solvents such as *N*,*N*-DMAc, DMF, NMP, and to some extent in THF and DMSO and are insoluble in organic solvents such as chloroform, acetone, and benzene. Because of the presence of —Si—O— flexible linkage, these polymers show good solubility as well as good thermal stability.

Thermal Properties

The thermal stability of PAI5, PAI10, and PAI12 were evaluated by means of TGA in a nitrogen atmosphere at a heating rate of 20°C/min. The TGA data of above mentioned polymers were compared with PAI prepared in NMP as organic solvent. Thermal stability of the polymers were compared based on 5 and 10% weight loss (T5, T10) of the polymers and their residue at 700°C (char yield). TGA data reveal that thermal degradation of PAIs was not started up to 230°C and their residue at 700°C is

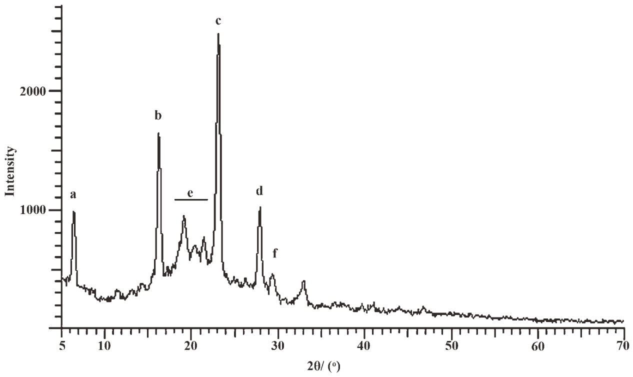


Figure 5. WAXS diffractogram of PAI10.

about 40%. The thermo analysis data of these polymers are summarized in Table VI. According to these data, it can be inferred that the resulting polymers are thermally stable. Figure 3 shows the TGA thermograms of these PAIs.

T5, T10, char yield, and T_g of PAI_{NMP} were observed at 270, 290, 40%, and 96°C, respectively. Relatively higher T5, T10 of this polymer may be due to its higher molecular weight.

Char yield can be applied as criteria for estimating limiting oxygen index (LOI) of the polymers in accordance with Van Krevelen and Hoftyzer equation.[41,54]

"LOI = 17.5 + 0:4 CR

where CR = char yield at 800°C."

Calculated LOI values of PAI12, PAI5, and PAI10 were 30.3, 33.1, and 33.5, respectively. On the basis of LOI values, such macromolecules can be considered as self-extinguishing polymers, especially PAI10.

The thermal behaviors of PAI5, PAI10, and PAI12 were studied by DSC. It can be seen that almost glass transition temperatures of all polymers (T_g) observed around 100°C. It can be said that the presence of Si flexible linkage in polymer back bone resulted in increasing processability of PAIs by decreasing their glass transition temperatures below polymer's decomposition temperature (Figure 4).

WAXS Study

WAXS measurements were performed for PAI10 (Figure 5). The percentage of crystallinity was calculated through graphical integration of the diffracted intensity data in the 2θ range 5–50° and subtraction of the amorphous scattering band intensity.

Diffraction patterns for PAI-Si show four main crystalline regions. WAXS patterns of PAI10 shows crystal reflection patterns at a, b, c, and d regions with maximum at about $2\theta = 6.3$, 16.3, 23, and 27.8, respectively. It also shows broad diffusion scattering patterns with maximum at $2\theta = 19°$ and 29°, at e and f regions. The percentage of crystallinities obtained for PAI10 at a, b, c, and d regions are about 7, 12, 17, and 7%, respectively. The observed total crystallinity of PAI10 was about 43% which was higher than total crystallinity of PAI_{NMP} which was about 36%. It can be inferred that polymerization in a NVOS resulted in better arrangement of polymer chains in a neat orderly manner.

Dielectric Constants of Polymers

The dielectric constant of thin film of PAI10 was measured with an optical method and calculated via Maxwell's identity ($\varepsilon = \eta 2$, $\Delta\varepsilon = +0.3$). Its η_i, η_o, and ε_o, were 1.53, 1.46, and 2.5, respectively. η_i, η_o, and ε_o are defined as in-plane refractive index, out-of-plane refractive index, and out-of-plane dielectric constant, respectively. The difference between the in-plane and out-of-plane refractive indices was about 0.07 which can be a good estimation of the anisotropy of the system. Its dielectric constant, 2.5, was lower than common siloxane-free polyimides or polyamides ($\approx$3). This was related to the reduced polarity of PAI-Si due to the incorporation of siloxane units into the polymer backbone. As dielectric constant indicates the ability of an insulator to store electrical energy, these thermally stable polymers showed preliminary requirements for application as electrical insulators in electronic industry.

CONCLUSION

In this work, we successfully synthesized moderate to high molecular weight siloxane modified PAIs. These new PAIs-Si were synthesized from direct polycodensation reaction of a new siloxanic dicarboxylic acid having a preformed imide ring and MDI. They were prepared according to the isocyanate route under microwave irradiation in different ILs and NVOSs. We have developed an efficient, convenient, and practical approach for the synthesis of thermally stable PAI-Sis using microwave irradiation in conjunction with ILs/NVOS. Joining advantages of microwave irradiation and ILs/NVOS brought about polymerization reactions with safe operation, low pollution, and rapid access to products and simple workup. This environmentally friendly green technique is a fast, high yielding and simple manipulation route, which avoids the usage of VOSs and catalysts. Moreover, in comparison with common methods for preparation of polyamides, we omit one stage for preparing diacyl chloride from diacid, or use of dehydrating agents and VOS needing for direct polyamidation. Conversely, the introduction of siloxane flexible linkage together with amide, and imide functions in polymer back bone resulted in structural features which have brought about macromolecular rigidity and crystallinity, accompanying enhanced solubility and low T_g of the resulting polymers. Therefore, these structural characteristics make these polymers thermally stable as well as process-able. Polymer films can be easily form via solution casting and they can be easily soften and form after putting them in boiling water. They revealed good thermal stability, improved solubility, and reduced dielectric constant that imply to their potential capability as electrical insulators as well.

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