Polymers from Renewable Resources. XII. Structure Property Relation in Polyamideimides from Rosin

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Synopsis

Polyamideimides were synthesized from rosin maleic anhydride adduct either by reacting the acid chloride of the latter with different diamines or by self-polycondensation of rosin imido amino acid in the presence of thionyl chloride. The rosin imido amino acids were prepared by condensing rosin-maleic anhydride adduct with diamines. The presence of lithium chloride was found to have pronounced effect on yield and molecular weight of the polymers. The poly-amideimides were characterized by infrared, elemental analysis, and viscosity measurements. The polymers were either amorphous or poorly crystalline in nature and soluble only in highly polar solvents. The thermal stability of the polymers has been studied. Some generalizations about structure-property relation in polyamideimides were made.

INTRODUCTION

Petroleum-based trimellitic anhydride (TMA), benzophenone tetracarboxylic dianhydride (BTDA), and pyromellitic dianhydride (PMDA) are the key chemicals for the manufacture of a number of industrially important chemicals and high performance polymers such as polyimides polyamideimides, polyesterimides and other copolyimides, high temperature plasticizers, etc. Recently, a number of copolyimides based on rosin-maleic anhydride dielesalder adduct (RMA) have been reported from this laboratory.[1-11]

To successfully develop any material, particularly polymers, and to meet the exacting specifications of the end uses, an understanding of how the structure of the material relates to its properties and behavior is essential. In the present paper we wish to report the synthesis of some new polyamideimides and the study on their structure-property relation.

EXPERIMENTAL

Reagents

Rosin used has the following specifications: melting point 56°C; acid number 162.8; specific gravity 1.06. Maleic anhydride (Adarsh Chemicals & Fertilizers Ltd.) was purified by sublimation. Ethylenediamine (SD) and hexamethylenediamine (Fluka) were purified by distillation under reduced pressure (~ 20 torr) in nitrogen atmosphere. p-Phenylenediamine (E. Merck), 4, 4'-diaminodiphenyl sulfone (Wilson), and 4, 4'-diaminodiphenyl-methane (E.

Merck) were crystallized from ethanol. 4, 4'-*Bis*(aminocyclohexyl) methane (DuPont) was used as received.

All other chemicals like thionyl chloride (Ranbaxy) triethylamine (Sarabhai Chemicals), *N-N*-dimethyl formamide (SRL), and *N*-methyl-2-pyrrolidone (NMP) (Fluka) were purified by following standard procedures.[12]

Monomers

RMA[3,4] and monoacid chloride of RMA (RMA-Cl)[6] were prepared by the procedures reported earlier.

Synthesis of Rosin-Imido-Amino Acid (RIAA). RIAA was synthesized by condensing RMA with a diamine. The detailed procedure was reported earlier.[7] The diamines used were 4, 4'-diaminodiphenylsulfone and 4, 4'-*bis* (aminocyclohexyl)methane. Reaction conditions were almost identical except that 1 h is the reaction time when 4, 4'-*bis*(aminocyclohexyl)methane was used whereas 2 h are necessary for the other diamine. Since 4, 4'-diaminodiphenylsulfone was insoluble in diethyl ether the final product (RIAA) was washed with a 1 : 1 water/alcohol mixture (v/v).

Polymer Synthesis

Polymer synthesis was carried out by two methods.

Method A: Synthesis from RIAA. Self-polycondensation of RIAA to polyamideimide was carried out in various aprotic solvents with or without LiCl following the procedure reported earlier.[6]

Method B: Synthesis from RMA-Cl. Polyamideimides were prepared by reacting RMA-Cl with a diamine in dimethyl formamide (DMF) solution according to the procedure reported earlier.[6] Other solvents were used in place of DMF in a few syntheses.

Polymer Characterization

Viscosity Measurements. Inherent viscosity of the polymer samples was measured in 0.5% (g/mL) solution in DMF at 30°C using a Ubbelohde suspended level viscometer.

Density Measurements. The density of the polymer samples was determined by means of a small pyconometer in dry benzene at 30°C.

Infrared (IR) Spectroscopy. Infrared spectra of all the polymer samples were recorded with a Perkin-Elmer 237B spectrophotometer on KBr pellets.

X-Ray Measurements. Wide-angle X-ray diffraction diagrams were recorded with a Dorn-1 X-ray diffractometer using Ni-filtered CuK$_\alpha$ radiation.

Thermal Analysis

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) of the polymers were recorded simultaneously with a Mom Derivatograph of a Paulik Paulik-Erdey system in air at a heating rate of 10°C/min.
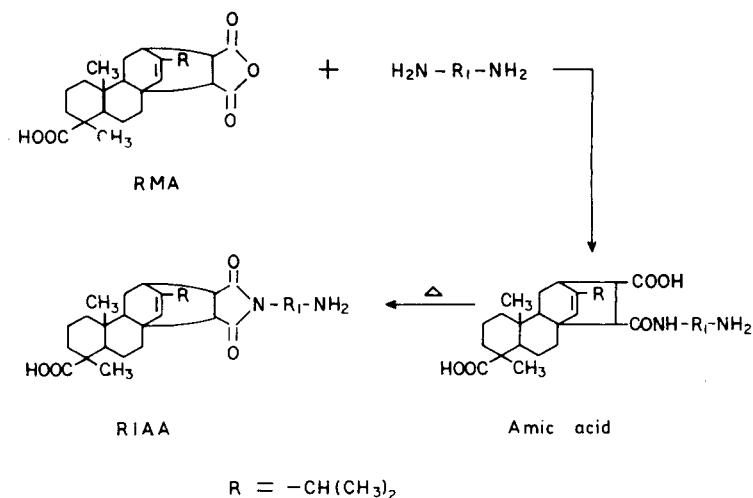
Fig. 1. Reaction scheme for synthesis of RIAA.

Isothermal Aging

Polymer samples (0.5 g each) were heated in a specially designed air-circulating aging oven at different temperatures. The weight loss in air was recorded at different time intervals.

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

Reaction scheme for the synthesis of RIAAs is shown in Figure 1. Structure of the amino acids (RIAAs) was confirmed by elemental analysis (Table I) and IR spectroscopy (Table II). Physical characteristics of these acids are shown in Table I. These amino acids are soluble in methanol, ethanol, tetrahydrofuran (THF), dioxane, acetone, ethylmethylketone, cyclohexanone, DMF, NMP, dimethylacetamide (DMAC), dimethylsulfoxide (DMSO), m-cresol, acetic acid, and insoluble in n-hexane, cyclohexane, ethyl acetate, amyl acetate, diethyl ether, and carbon tetrachloride.

TABLE I
Yields and Physical Properties of the Rosin-imido-amino acids

RIAA	Diamine component	Color	Melting point (°C)	Yield (%)	Elemental analysis (Nitrogen)	
					Calcd.	Found
RIAA-1	Ethylenediamine	Light brown	170	92	6.33	6.18
RIAA-2[a]	Hexamethylene diamine	Light brown	125	93	5.60	5.44
RIAA-3[b]	p-Phenylene diamine	Light brown	210	90	5.71	5.65
RIAA-4[c]	4,4'-Diamino diphenyl methane	Light brown	130	90	4.72	4.61
RIAA-5	Diaminodiphenyl sulfone	brown	160	86	4.44	4.35
RIAA-6	4,4'-Bis(amino cyclohexyl)methane	Light brown	127	96	4.72	4.61

[a] From ref. 6.
[b] From ref. 7.
[c] From ref. 10.

TABLE II
Characteristic Absorption Bands in IR Spectra of the Rosin-imido-amino acids

RIAA	Characteristic IR Absorption Band Appeared for				
	Imide functionality at (cm^{-1})	$>$C$=$O of —COOH functionality at (cm^{-1})	—OH stretching of —COOH and —NH— stretching of —NH$_2$ functionality at (cm^{-1})	Olefinic double bond at (cm^{-1})	Sulfone functionality at (cm^{-1})
RIAA-1	725 (m), 1725 (s) and 1775 (m)	1690 (s)	3260–3400 (m)	1625 (w)	—
RIAA-2	725 (m), 1725 (s) and 1785 (m)	1690 (s)	3000–3500 (m)	1630 (w)	—
RIAA-3	725 (m), 1725 (s) and 1785 (m)	1700 (s)	3000–3500 (m)	1630 (w)	—
RIAA-4	725 (m), 1725 (s) and 1785 (m)	1690 (s)	3375–3475 (m)	1625 (w)	—
RIAA-5	725 (m), 1725 (s) and 1785 (m)	1695 (s)	3350–3450 (m)	1620 (w)	1110 (s) and 1290 (s)
RMA-6	725 (m), 1725 (s) and 1775 (m)	1640 (s)	3200–3400 (m)	1620 (w)	—

s, m, and w indicate strong, medium, and weak intensity of the IR absorption bands.

Polymer Synthesis and Characterization

Reaction scheme for the synthesis of polyamideimide from rosin is shown in Figure 2. Initially, the reaction temperature was kept low to allow complete amidation, preventing the premature occurrence of imidization of the resulting amic acid due to the liberated water molecules during imidization which may cause hydrolysis of the acid chloride group and other undesirable side reactions. That perhaps explains the formation of an insoluble product when

Fig. 2.   Reaction scheme for synthesis of polyamideimide from rosin.

RIAA was melt polymerized.[6] Insolubility of the polymers is due to the onset of crosslinking at elevated temperatures, which was discussed earlier.[11] In this method of synthesis there is also a possibility of formation of either head to head and tail to tail or head to tail linkage.

In an attempt to increase the molecular weight of the polymers, polymerization reactions were carried out in different reaction media. Different solvents, mixed solvents, and metal salt solutions were used as reaction media. Suitable solvents or mixed solvents have been used with the intention of increasing the solubility of the polymer in the reaction medium; otherwise the polymer may precipitate out and be incapable of further growth. However, by using different solvents or mixed solvents, molecular weights (inherent viscosities) could not be increased appreciably by method A. This is perhaps due to the difficulty in converting acid to acid chloride due to steric hindrance.[13]

When lithium chloride was added to the reaction medium, yield and molecular weight of the polymer obtained by method A were found to decrease. But the presence of lithium chloride enhanced the reaction between an acid chloride and a diamine in method B. Perhaps lithium chloride in

method A may retard conversion of RIAA to its acid chloride derivative by thionyl chloride.

In method B slight improvement in the yield and inherent viscosity of the polymer formed was observed when NMP was used as the solvent. The mixed solvent (DMF : NMP = 3 : 1) produced the same effect as pure NMP. When

TABLE III
Yields and Physical Characteristics of the Polyamideimides from Rosin

Polymer	Method of polymerization	Yield (%)	Color	Inherent viscosity (dL/g)[a]	Molecular weight ($\overline{M}_n$) from VPO	Density (g/cc)	T_g^d (°C)
PAI-1	A[b]	85	Brown	0.28	—	—	265
	B[c]	(92)76	Brown	(0.33)0.25	(13,500)	(1.33)	
PAI-2	A[b]	85	Brown	0.30	—	—	260
	B[c]	(92)78	Brown	(0.35)0.27	(14,000)	(1.34)	
PAI-3	A[b]	80	Deep brown	0.15	—	—	285
	B[c]	(91)74	Deep brown	(0.31)0.15	—	(1.35)	
PAI-4	A[b]	78	Deep brown	0.15	—	—	280
	B[c]	(91)74	Deep brown	(0.31)0.14	(13,000)	(1.36)	
PAI-5	A[b]	77	Deep ash	0.15	—	—	275
	B[c]	(90)70	Deep ash	(0.28)0.15	—	(1.32)	
PAI-6	A[b]	82	Deep brown	0.32	—	—	280
	B[c]	(93)70	Deep brown	(0.37)0.28	(16,500)	(1.30)	

[a] Measured with 0.5% (w/v) solution in DMF at 30°C.

[b] With NMP as the reaction medium.

[c] In this process the values within and without parentheses correspond to those obtained in the reaction using DMF : NMP = 3 : 1 containing 4% LiCl and DMF as the reaction medium, respectively.

[d] From DTA curve (Fig. 4).

TABLE IV
Characteristic Absorption Bands in the IR Spectra of the Polyamideimides from Rosin

Polymer	Characteristic IR absorption band appeared for				
	Imide functionality at (cm^{-1})	$>$C=O of —CONH— functionality at (cm^{-1})	—NH— stretching of —CONH— functionality at (cm^{-1})	Olefinic double bond at (cm^{-1})	Sulfone functionality at (cm^{-1})
PAI-1	725 (m), 1725 (s) and 1775 (m)	1550 (s) and 1640 (s)	3200–3400 (m)	1625 (w)	—
PAI-2	725 (m), 1725 (s) and 1785 (m)	1540 (s) and 1675 (s)	3300–3400 (m)	1625 (w)	—
PAI-3	725 (m), 1725 (s) and 1775 (m)	1550 (s) and 1640 (s)	3300–3500 (m)	1630 (m)	—
PAI-4	725 (m), 1725 (s) and 1775 (m)	1550 (s) and 1640 (s)	3200–3500 (m)	1625 (w)	—
PAI-5	725 (m), 1725 (s) and 1775 (m)	1550 (s) and 1640 (s)	3300–3500 (m)	1625 (w)	1110 (s) and 1290 (s)
PAI-6	725 (m), 1725 (s) and 1775 (m)	1550 (s) and 1640 (s)	3200–3500 (m)	1620 (w)	—

s, m, and w indicate strong, medium, and weak intensity of the IR absorption bands.

lithium chloride was added to the reaction medium the yield and viscosity of the polymers were increased with the increase in concentration of lithium chloride in pure or mixed solvent systems. The optimum concentration of metal salt is 4–6%. But higher percentage ($> 4\%$ w/v) of the salt causes a decrease in yield and molecular weight of the polymer produced. It has been reported that the addition of metal salts such as lithium chloride or calcium chloride to a reaction medium has a similar effect on the molecular weight of the polymer.[14,15] The mixed solvent DMF : NMP (3 : 1) containing 4% lithium chloride was the best reaction medium for method B (Table III). It appears that LiCl enhances the basicity and solubilizing power of the solvent by forming a complex with the solvent molecules.[16,17] Thus the comparatively lower basic aromatic amines become more effective in the presence of LiCl than aliphatic or cycloaliphatic ones. There is also a possibility of formation of a complex between lithium chloride and RMA-Cl and/or diamine which facilitates the polycondensation. The problem of steric hindrance as in the case of self-polycondensation of RIAA in the presence of thionyl chloride is absent here because acid has already been converted to acid chloride.

The structure of repeat unit of the polymers was confirmed by elemental (N_2) analyses (Table III) and IR spectroscopy (Table IV). Some physical characteristics of the polymers are shown in Table III.

Polymer Properties

The polymers are soluble in highly polar solvents like m-cresol, DMF, DMAC, DMSO, NMP, HMPA and sparingly soluble in THF, 1.4-dioxane, and cyclohexanone. Solubility of the polymers follows the order: PAI-5 > PAI-1 $\approx$ PAI-2 > PAI-4 $\approx$ PAI-6 $\approx$ PAI-3. This is consistent with the decreased solubility of para-linked polymers and increased solubility of polymers containing sulfone group. This behavior is related to the chain packing in the polymer lattice which in turn controls the degree of crystallinity in polymers.

The influence of chain packing is also reflected in the wide-angle X-ray diffraction (WAXD) of the polymers (Fig. 3). Most of the polymers are amorphous except PAI-2 and PAI-3, which have some degree of crystallinity. The large rosin moiety in the polymer repeat unit makes the rosin polymers usually amorphous or poorly crystalline. The symmetry of the diamine unit partially helps to bring some degree of order in the macromolecules. However, different conformations of the cyclohexyl ring of the diamine in PAI-6 decreases the chain symmetry compared to hexamethylene diamine (PAI-2)-based polymer.

Thermal Behavior

Infrared spectra of the heat-treated polymer samples are similar to those of the virgin polymers except that the absorption band due to olefinic double bond at 1620–1630 cm^{-1} is absent. This is possibly due to crosslinking. Crystallinity as evidenced from WAXD of the heat-treated samples, in general, is higher than that of the virgin polymers which may be due to crosslinking. Heat treatment of the polymers near their melting points also induces order in the polymer chain, resulting in a higher degree of crystallinity.[18,19]
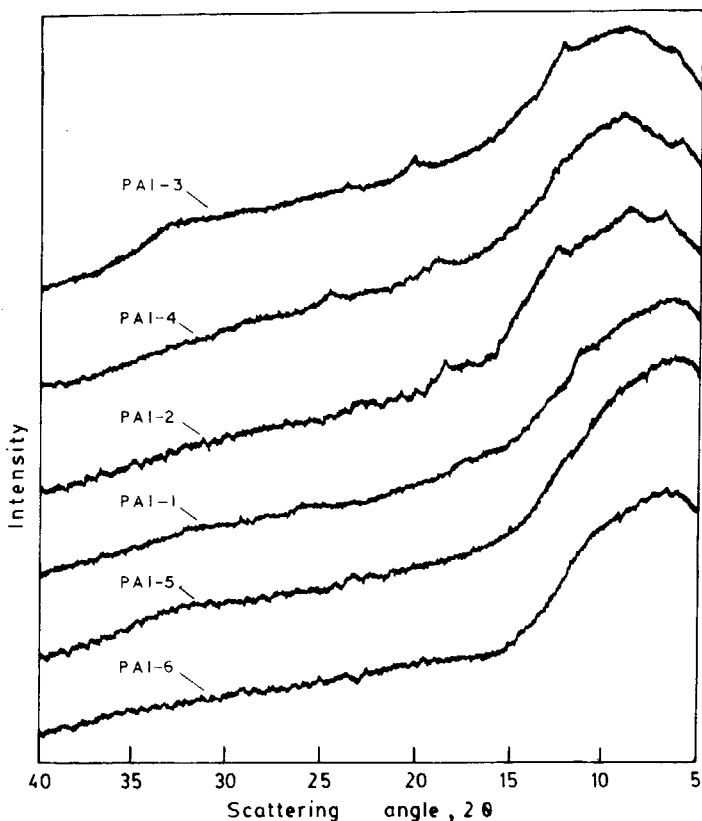
Fig. 3. X-ray diffraction diagram of the polymers from rosin.

The heat-treated polymer samples are insoluble in all the solvents in which the polymers are soluble prior to heating. Insolubility of these heat-treated samples may be due to either increased molecular weight of polymers by chain extension or crosslinking reaction with the formation of three-dimensional network, or both.

DTA and TGA curves of the polymers are shown in Figure 4. PAI-1 and PAI-2 have the lowest T_g, possibly due to the presence of aliphatic amine moiety in the polymer chain. The highest T_g of PAI-3 is due to the rigid *para*-phenylene diamine structure of the polymer. The exothermic peaks which actually indicate thermal decomposition occur at around 300°C for the polymers containing aliphatic chain, and at about 345°C for those containing aromatic and cycloaliphatic ring system in the macromolecular chain.

The polymers suffer no weight loss up to and above 250°C. For example, PAI-3 is stable to 335°C while PAI-4 and PAI-6 suffer no weight loss up to 315°C or 325°C, respectively. It appears that the thermal stability of the polymers follows the order PAI-3 > PAI-4 ≈ PAI-6 > PAI-5 > PAI-1 > PAI-2. These are consistent with the higher thermal stability of benzene ring and greater chain symmetry of para-linked polymer, and the lower thermal stability of aliphatic chains. Oxidative degradation studies showed that the site of initial attack is the C—H bond nearest to the —NH— group and the
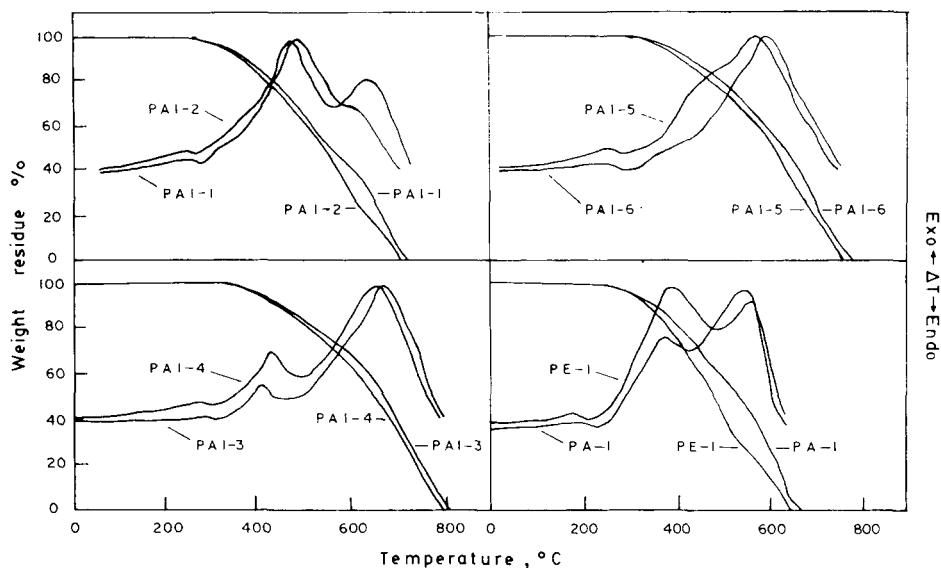
Fig. 4. Differential thermal analysis and thermogravimetric analysis of polymers from rosin in air and at a heating rate of 10°C/min.

absence of a hydrogen atom directly linked to this carbon atom accounts for the markedly superior oxidative stability.[20] Absence of such C—H bond in PAI-3, PAI-4, and PAI-5 improves the thermal stability of the polymer.

Isothermal aging of the polymers was carried out at 200, 225, 250, 275, and 300°C in air for 36 h. No weight loss occurred at 200°C in air even after 36 h for all the polymers. For PAI-3 to PAI-6, no weight loss occurred up to 275°C in 36 h. Results of isothermal aging of the polymers at 225, 250, 275, and 300°C in air are summarized in Table V. The weight losses appear to be

TABLE V
Isothermal aging of the Polymers from Rosin in Air

Isothermal aging temperature (°C)	Polymer	Cumulative weight loss (%) after (h)					
		2	4	8	12	24	36
225	PAI-1	1.12	1.12	1.46	1.75	1.98	2.20
	PAI-2	1.30	1.30	1.62	1.93	2.21	2.45
	PAI-3 to PAI-6	0	0	0	0	0	0
250	PAI-1	1.95	2.15	2.30	2.75	3.05	3.35
	PAI-2	2.05	2.35	2.92	3.32	3.76	4.15
	PAI-3 to PAI-6	0	0	0	0	0	0
275	PAI-1	2.55	3.05	3.50	3.90	4.95	6.25
	PAI-2	2.80	3.30	3.90	4.75	5.95	7.45
	PAI-3 to PAI-6	0	0	0	0	0	0
	PAI-1	5.15	6.24	6.98	7.56	9.11	11.20
	PAI-2	5.70	7.10	8.04	8.96	10.90	13.25
300	PAI-3	2.70	3.05	3.45	3.70	4.55	5.05
	PAI-4	3.15	3.50	3.82	4.12	5.04	6.06
	PAI-5	3.50	3.87	4.42	4.80	5.75	7.05
	PAI-6	3.08	3.44	3.87	4.15	4.98	6.05

significant at and above 275°C for PAI-1 and 2, while the remaining polymers are fairly stable. Isothermal aging data also indicate that PAI-3 is the most thermally stable while PAI-4 to PAI-6 have comparable thermal stability but somewhat lower than that of PAI-3 (Table V). The effect of prolonged heating at a constant temperature on polymer has been studied. PAI-3 on heating at 180°C for 1000 h in air showed 13% weight loss.

Lawrence and co-workers prepared a polyamideimide by reacting dihydro-maleopimaric acid with 4, 4'-diaminodiphenyl methane, and observed that the polymer showed 10% and 25% weight loss at 390 and 460°C in air.[21,22] TGA of the same polymer underwent 6% and 11% weight loss at 400 and 425°C in air, respectively.[23] We have observed that PAI-4 nearly identical with the above polyamide-imide exhibited 6% and 9% weight loss, respectively, under the above conditions. The resistance to thermal degradation of rosin polymers appears to be due to the condensed hydrophenthrene ring of rosin which may undergo crosslinking through its residual double bond at higher temperatures.

CONCLUSION

The present study points out a few generalizations on the structure-property relation in polyamideimides derived from rosin. Although rosin is a plant exudate of poor thermal stability in itself, it can be converted into a series of fairly thermally stable and easily processable polymers. The residual double bond in rosin polymers may be utilized in crosslinking, resulting in further enhancement of thermal stability. This is a premium point not available in trimellitic anhydride-based polyamideimides.

The solubility, thermal stability, and T_g are all related to the polymer structure. The presence of para linkages in the benzene rings ensures higher degree of chain symmetry resulting in higher degree of crystallinity which in turn makes the polymer less soluble and thermally more stable with higher T_g values. Such observations were also reported in other polymers earlier.[24,25]

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