

Synthesis and Characterization of Benzimidazole-Based Low CTE Block Copolyimides

Shafiq urRehman, GuangLiang Song, He Jia, HongWei Zhou, XiaoGang Zhao, GuoDong Dang, ChunHai Chen

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China

Correspondence to: G. Dang (E-mail: dgd_tong@jlu.edu.cn)

ABSTRACT: A series of block and random copolyimide films were synthesized from various molar ratios of two diamines, rigid 2-(4-aminophenyl)-5-aminobenzimidazole (APBI) and flexible 4,4'-oxydianiline (ODA) by polycondensation with dianhydride 3,3',4,4'-biphenyltetracarboxylic dianhydride. The contents of APBI ranged from 10 to 60 mol % in copolyimides. The copolyimide films obtained by thermal imidization of poly(amic acid) solutions, were characterized by TMA, DMA, TGA, DSC, wide-angle X-ray diffraction, FTIR, tensile testing, water uptake (WU), and dielectric constant measurements. Rigid heterocyclic diamine APBI with inter-chain hydrogen bonding capability, led to low coefficient of thermal expansion (CTE), high T_g , high thermal stability and better mechanical properties. Increasing the APBI mol % caused a gradual decrease in the CTE and increase in T_g , thermal stability and tensile strength properties of the copolyimides films. Moreover, significantly enhanced thermal and mechanical properties of the block copolyimides were also found as compared to random copolyimides. The block copolyimide with APBI content of 60 mol %, achieved excellent properties, that is, a low CTE (4.7 ppm/K), a high T_g at 377°C, 5% weight loss at 562°C and a tensile strength at 198 MPa. This can be interpreted because of comparatively higher degree of molecular orientation in block copolyimides. These copolyimides also exhibited better dielectric constant and WU. This combination of properties makes them attractive candidates for base film materials in future microelectronics. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 2561–2570, 2013

KEYWORDS: CTE; block copolyimides; polybenzimidazole; thermal properties

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INTRODUCTION

Aromatic polyimides (PIs) are an important class of polymers used extensively in a variety of high performance materials and composites because of their outstanding physical properties considerably high glass transition temperatures, high resistance to chemicals, and radiations, comparatively low dielectric constants, and superior mechanical properties. Some wide-ranging applications of aromatic PIs include microelectronics, optoelectronics, automotive, aerospace engineering, advance textiles, and membranes technology. The recent trend is the development of multifunctional aromatic PIs that will attain all desired application-dependent properties simultaneously.^{1–5}

Recently, a high demand for PI films as base film materials has been seen in electronic devices like flexible printed circuit boards, tape-automated bonding, and chip-on-film assembly, and so forth.^{6–10} The most desirable feature for this type of PI films is the low linear coefficient of thermal expansion (CTE). Low CTE PI films demonstrate the better thermo-dimensional stability against the heat cycles during the circuit board fabrication proc-

esses.^{11–13} Common PIs having high CTE values (40–80 ppm/K) undergo significant curling due to CTE mismatch between PI and copper (~18 ppm/K) in dielectric layers. In past decades, many research efforts have been focused on the development of low CTE PI systems without deterioration of other excellent properties. Some common approaches include PI/Inorganic composites (nanocomposites, fillers, etc.), use of a stiff, rigid rod like backbone structure, copolymerization techniques, fluorinated low CTE and dielectric constant PIs, and so forth. However, little has been elucidated about the thermal expansion behavior of block copolyimides. Besides thermal stability and excellent mechanical properties, low dielectric constant and moisture absorption are also very important in future microelectronic applications.^{9,14–16}

Block copolymers are major class of polymeric materials that possess the potential to achieve the desired characteristics, functionalization, and molecular architectural control. Block copolymerization offers several advantages over random copolymerization because the molecular architecture can be tailored to develop the materials with desirable structure and the

functionality. It may offer a broader spectrum of properties to meet the demands of various applications.^{17–21} The desired properties achieved by block copolymerization cannot be obtained by random copolymerization, despite the fact that other parameters kept constant in both cases.^{22–24}

Polybenzimidazoles (PBIs) are well-known high performance polymers because of their excellent capability to withstand harsh conditions without any major effect on properties. These are widely used in aerospace industry where prime requirements are thermal stability, high strength, and corrosion resistance.^{25,26} Some efforts have been made to combine the PBI and PI to develop PBI-PI copolymers to achieve required characteristics.^{27–30}

This paper describes the synthesis and characterization of benzimidazole based block and random copolyimides. These copolyimides were successfully synthesized from the copolymerization of rigid rod-like heterocyclic diamine 2-(4-aminophenyl)-5-aminobenzimidazole (APBI) and flexible 4,4'-Oxydianiline (ODA) with dianhydride, 3,3',4,4'-biphenyltetracarboxylic dianhydride (sBPDA). Six block copolyimide films were prepared with systematic variation of block length and block contents of both rigid (APBI-sBPDA) and semi-flexible (ODA-sBPDA) blocks. Thermal and mechanical strength properties of block copolyimides were optimized by controlling block length and contents.

EXPERIMENTAL

Materials

APBI and ODA were supplied by Sinopharm Chemical Reagent sBPDA (mp. 306°C) was obtained from Beijing Jiaohua Co., and dried in vacuum at 200°C for 2 h before use. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced before use.

Synthesis of the Copolyimides

Block Copolyimides. The block copolyimides were synthesized by the two-pot procedure.^{17,22,31,32} A typical polymerization procedure for preparation of 50 : 50 mol % APBI/ODA block copolyimide, is mentioned here. In one flask, 1.7947 g (6.1 mmol) of sBPDA was gradually added to a stirred mixture of 1.3456 g (6 mmol) of APBI in 30 mL of DMAc. This mixture was stirred for 4 h at room temperature under nitrogen to obtain dianhydride-terminated poly(amic acid) (PAA) oligomer with solid content of 10%. Similarly, in another flask diamine-

terminated PAA oligomer was prepared by gradual addition of 1.1475 g (3.9 mmol) of sBPDA to a stirred mixture of 0.8010 g (4 mmol) of ODA in 20 mL of DMAc. This mixture was also stirred for 4 h at room temperature. Both PAA solutions were mixed and stirred for 3 h under nitrogen, to prepare viscous block copoly(amic acid) precursor solution. This solution was spread onto a flat glass plate using a doctor blade. Glass plate was thermally treated at 80°C for 1 h, 100°C for 1 h, 150°C for 1 h, and 180°C for 1 h in ventilated oven to remove the solvent, and then heated at 250°C for 1 h, 320°C for 1 h, and 400°C for 1 h in vacuum oven to get a thermally imidized block copolyimide film. After soaking in water, the film was peeled off from the glass plate and dried. The synthesis details of block copolyimides are given in Table I and Scheme 1.

Random Copolyimides. A typical polymerization procedure for the preparation of 50 : 50 mol % APBI/ODA random copolyimide, is presented here. In a flask, 1.0012 g (5 mmol) of ODA and 1.1213 g (5 mmol) of APBI were dispersed in 50 mL of DMAc and mixture was stirred. 2.9422 g (10 mmol) of sBPDA was gradually added to stirring mixture of APBI and ODA. Then, mixture was further stirred for 7 h at room temperature under nitrogen to obtain viscous random copoly(amic acid) solution. Then film was cast and thermally cured in the same way as given above for block copolyimide film. The details of random copolyimides synthesis are described in Table II.

A homopolyimide sBPDA/ODA was also prepared under the same conditions.

Characterization

CTE of the films was measured using a thermomechanical analyzer TMA/SDTA841e (Mettler Toledo) at a temperature increase of 5°C/min. CTE data were collected from the second heating run after the first heating run which was carried out to eliminate the absorbed moisture. This practice is very important to get correct CTE curves with linear film elongation. Dynamic mechanical analysis (DMA) was performed using a TA Instruments DMA Q800 at 5°C/min and 1 Hz. The film geometry was in tension mode. Glass transition temperature (T_g) is reported as the temperature corresponding to the maximum of $\tan\delta$ curve. Differential scanning calorimetric (DSC) measurements were taken in TA instruments DSC Q100 using a scan

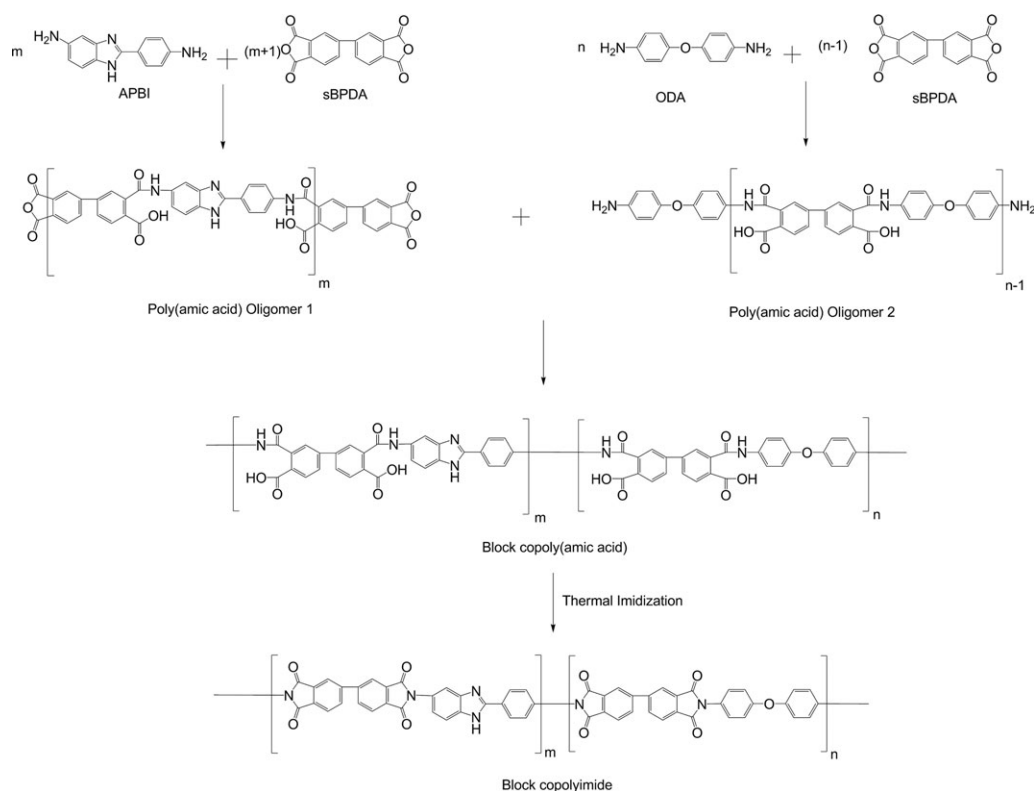
Table I. Preparation of Block Copolyimides

PI	Block composition		Monomer feed (mmol)		(APBI/ODA) ^c molar ratio (%)	APBI contents (wt %)
	<i>m</i>	<i>n</i>	(sBPDA/APBI) ^a	(sBPDA/ODA) ^b		
B1	10	90	1.1/1.0	8.9/9.0	10 : 90	11
B2	20	80	2.1/2.0	7.9/8.0	20 : 80	22
B3	30	70	3.1/3.0	6.9/7.0	30 : 70	32
B4	40	60	4.1/4.0	5.9/6.0	40 : 60	43
B5	50	50	5.1/5.0	4.9/5.0	50 : 50	53
B6	60	40	6.1/6.0	3.9/6.0	60 : 40	63

^a Poly(amic acid) oligomer 1.

^b Poly(amic acid) oligomer 2.

^c Block copoly(amic acid).



Scheme 1. Synthesis of block copolyimides.

rate of 10°C/min and a nitrogen flow rate of 50 mL/min. Tensile tests were performed at a constant crosshead speed of 8 mm/min. in a Shimadzu AG-I universal testing machine. Thermogravimetric analysis (TGA) was performed under inert atmosphere (N₂) in a 2050 Thermogravimetric Analyzer over the temperature range of 50–800°C at heating rate of 5°C/min. The thermal stability was evaluated in terms of 5% weight loss (T_d^5). Fourier transform infrared (FTIR) spectra were recorded on a Bruker Vector-22 FTIR spectrometer by casting the copolyimides films on KBr discs. The values of inherent viscosity (η_{inh}) were determined by Ubbelohde viscometer at 25°C using DMAc as a solvent, and copoly(amic acid) solution was given a concentration of 0.5 g/dL. Wide-angle X-ray diffraction (WAXD) patterns were recorded on Rigaku Wide-angle X-ray diffractometer. The 2 θ scan data were collected at 0.02° intervals over the range of 5–60° and the scan speed was 0.5° (2 θ)/min. Scanning electron micrographs (SEM) were observed on a Shimadzu SSX-550 microscope. Dielectric constants were measured using a Quadtech 1920 LCR precision meter at 1 MHz at a temperature of 25°C. Water uptake (WU) of the copolyimide films were measured by drying the film at 80°C under vacuum for 4 h until constant weight of dry film was obtained. Film was immersed into water at 25°C for 24 h. Then each film was taken out, quickly wiped with tissue paper to remove superficial water, and weighed on a microbalance. WU of the film was calculated as given below.

$$WU = [(M_w - M_d) / M_d] * 100 (\%)$$

where M_w and M_d are weights of water absorbed and dry films, respectively.

RESULTS AND DISCUSSION

Preparation of Copolyimides Films

Random and block copolyimides with various compositions were synthesized by thermal imidization. Scheme 1, Tables I and II summarizes the preparation details of block and random copolymerizations. Random copolyimides were prepared by one-step procedure. Therefore, all monomer sBPDA, APBI, and ODA were reacted together in DMAc at room temperature under nitrogen atmosphere to yield viscous random copoly(amic acid)s, which in turn converted into random copolyimides in the form of films. Block copolyimides were synthesized by two-pot procedure.^{17,22,31,32} In one pot, dianhydride terminated PAA oligomer was prepared by the reaction of APBI with a calculated excess of sBPDA in DMAc. In another pot, diamine terminated PAA oligomer was synthesized from a calculated excess of ODA with sBPDA in DMAc. After that, dianhydride

Table II. Preparation of Random Copolyimides

PI	Monomer feed sBPDA/APBI/ ODA (mmol)	APBI/ODA molar ratio (%)	APBI contents (wt %)
R1	10/1/9	10 : 90	11
R2	10/2/8	20 : 80	22
R3	10/3/7	30 : 70	32
R4	10/4/6	40 : 60	43
R5	10/5/5	50 : 50	53
R6	10/6/4	60 : 40	63

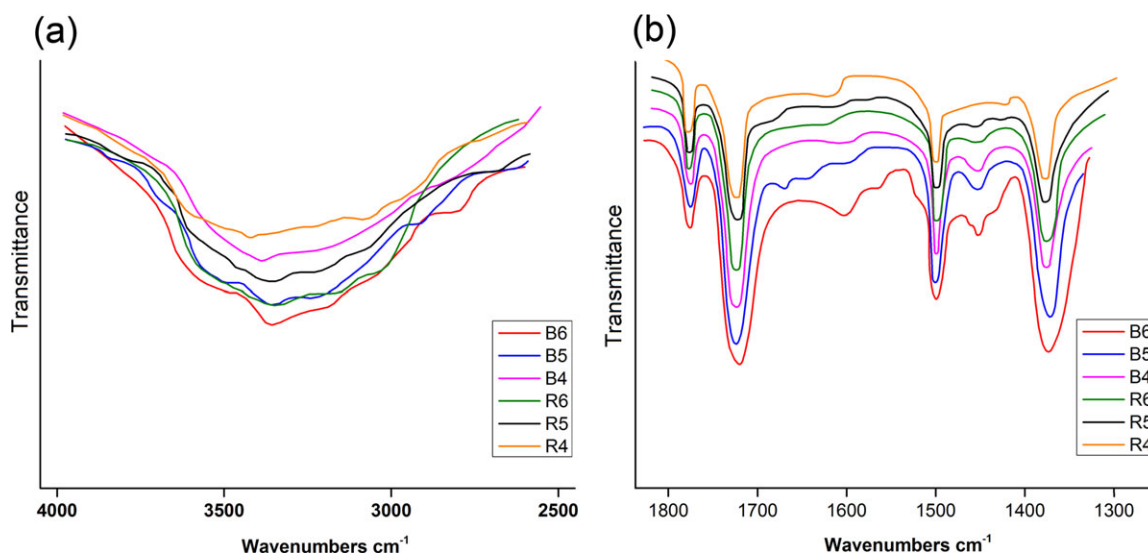


Figure 1. FTIR spectra of Copoly(amic acid)s. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

terminated PAA oligomer solution was gradually added to diamine terminated PAA oligomer solution, and they were reacted with each other to prepare block copoly(amic acid). All the copolyimide films were transparent and yellow or brownish-yellow in color over the whole composition range. Transparency of films indicates that two oligomer PAAs were well mixed via copolymerization. FTIR spectroscopy was used to monitor the structural characterization of the copolyimides and FTIR spectra are given in Figure 1. A broad stretching band of N—H groups was observed in the region of 3800–3000 cm^{-1} . Strong bands at 1780 and 1722 cm^{-1} due to the symmetric and unsymmetrical vibrations of the two carbonyl groups of imide rings, suggests the formation of imide ring. Aromatic conjugated C=C band was consistently appeared at 1500 cm^{-1} in all copolyimides spectra. Absorption band due to C—N stretching of imide rings was observed at 1377 cm^{-1} .

Inherent Viscosity

Inherent viscosity of oligomers PAAs, random and block copoly(amic acid)s was measured in DMAc at 25°C and presented in Table III. The inherent viscosity measurements of random and block copoly(amic acid)s indicates that molecular weights of all the copoly(amic acid)s were high enough to permit the casting of flexible and tough copoly(amic acid)s films. Copoly(amic acid)s were converted into tough copolyimide films by thermal imidization at elevated temperatures. The reactivity of monomer/oligomers, structure of monomers, polymer backbone, and prepolymer characteristics are the major factors affecting the extent of polymerization and viscosity. Copolymerization involves two different types of diamine/oligomers, which have different structure and reactivity.^{33–35} Polymerization of PAA is a nucleophilic reaction between dianhydride and diamine, which involves nucleophilic attack of amino group on the carbonyl carbon of anhydride group. Therefore, higher nucleophilicity of amine increase the reaction rate.^{36,37} APBI and ODA have different structures. In ODA, charge donor oxygen atom increases the charge density at amino nitrogen. However, in APBI, imidazole ring is in conjugation with benzene rings and charge transfer occurs from amino

group to conjugated system. Thus, APBI is less reactive than ODA. The effect of ODA reactivity is evident from the higher viscosity of oligo-2 PAA as compared to oligo-1 PAA and copoly(amic acid)s with higher ODA molar ratios. Inherent viscosity of copoly(amic acid)s decreased as ODA contents were reduced from 90 to 60 mol %. However, in high APBI contents (>40 mol %), inherent viscosity remained either stable or increased a little bit. Several authors investigated the effect of polymer backbone flexibility, polymer chain mobility, and stiffness on the inherent viscosity.^{34,38} In higher APBI molar ratios copoly(amic acid)s, rigidity of polymer backbone was the leading factor in polymerization. Rigid APBI increased the segmental rigidity of the polymer backbone resulting in increased viscosity.³⁸ The formation of block copoly(amic acid)s, is accompanied by viscosity increase after oligomer stage. Viscosity of block copoly(amic acid)s is either greater or equal to corresponding random copolyimides. This result infers the higher reactivity of diamine and dianhydride terminated oligomers to favor block copolymerization.

Thermal Properties

The thermal properties of random and block copolyimides were characterized by TMA, DMA, DSC, and TGA. CTE results are

Table III. Inherent Viscosity of Oligomers, Random and Block Copoly(amic acid)s

APBI/ODA molar ratio	Inherent viscosity (dL/g)			
	Random copoly (amic acid)s	Block copoly (amic acid)s	Oligo-1	Oligo-2
10 : 90	0.94	1.06	0.81	0.87
20 : 80	0.89	0.99	0.82	0.85
30 : 70	0.87	0.93	0.79	0.86
40 : 60	0.87	0.87	0.77	0.84
50 : 50	0.88	0.90	0.80	0.88
60 : 40	0.90	0.94	0.79	0.86

Table IV. Thermal Properties of Random and Block Copolyimides

Sample	CTE (ppm/K)	T_g (°C)		T_d^5 (°C) ^a
		DMA	DSC	
B1	41.3	294	282	515
B2	37.1	308	290	530
B3	31.0	323	301	543
B4	23.8	326	310	553
B5	16.7	352	331	558
B6	4.7	377	-	562
R1	46.2	285	274	503
R2	43.0	302	288	524
R3	37.5	318	296	537
R4	30.8	321	303	547
R5	25.1	338	313	548
R6	19.7	351	334	553
sBPDA/ODA	47.3	279	270	500

^aTemperature at which 5% weight loss was recorded by TGA.

reported in Table IV and Figure 2. The CTE of block copolyimides ranged from 4.7 to 41.3 ppm/K and that of random copolyimides ranged from 19.7 to 46.2 ppm/K. Block copolyimides showed lower CTE values than corresponding random copolyimides. The CTE is dependent on both backbone chemistry and the morphology and strongly influenced by molecular orientation. High molecular orientation aligns polymer chains axes parallel to the plane of the film often called “in-plane orientation,” results into low in-plane CTE.³⁹ In-plane orientation is correlated with the chain linearity/stiffness, degree of molecular packing (interchain interactions) and molecular mobility.^{9,40} Many researchers indicated that degree of chain orientation is higher for the PIs possessing rigid molecular structures as compared to flexible molecular structures or bulky side groups.^{9,15,39,40} Higher chain rigidity in PI systems causes a

drastic change in the in-plane orientation during thermal imidization.^{41,42} Therefore, CTE exhibit significant correlation with the rigidity in PI molecular structures. In this study, APBI was major contributor to polymer backbone rigidity in copolyimides. Low CTE values of copolyimides with the incorporation of APBI might originate from the rigid structure of APBI and the hydrogen bonding capability of benzimidazole rings. The CTE of copolyimides increased with the increase of flexible ODA contents. Both random and block copolyimides showed better CTE than homopolyimide sBPDA/ODA. The remarkably low CTE values of block copolyimides can be explained in terms of locally ordered microdomains in block copolyimides. These microdomains are not related to crystalline structure but based on highly oriented and well-ordered regions formed by rigid APBI blocks. Microdomains order increases with block length and become more random as block length decreases.⁴³ The highly oriented and well-ordered block copolyimide structure efficiently promoted molecular orientation in block copolyimides as compared to random copolyimides. This difference was further confirmed by WAXD patterns (Figure 5) of both types of copolyimides.

TGA thermographs are given in Figure 3 and T_g^5 in Table IV. All random and block copolyimides showed a similar decomposition behavior characterized by 5% weight loss (T_g^5) in the range from 503 to 563°C. All copolyimides thermally degraded in similar fashion in TGA curves. In the temperature range of 50–450°C, there is almost no weight loss. Above 490°C, weight loss started due to thermal decomposition of copolyimide backbone. The combined effect of heat resistant benzimidazole units and high rigidity led to better thermal stability of copolyimides. T_g^5 of copolyimides with 40 or higher mol % of APBI were well above than 540°C. B6 and R6 copolyimides with maximum APBI contents showed highest thermal stability. TGA data indicates that block copolyimides showed slightly higher T_g^5 than corresponding random copolyimides. This may be due to rigid APBI segments formation, leading to better packing and therefore to higher thermal stability.³¹

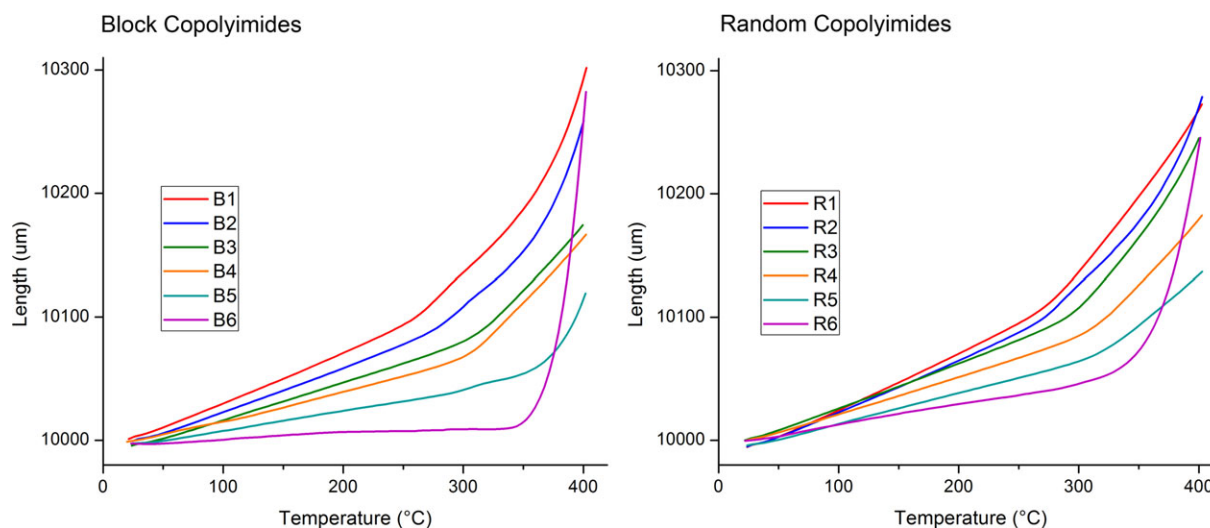


Figure 2. CTE curves of block and random copolyimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

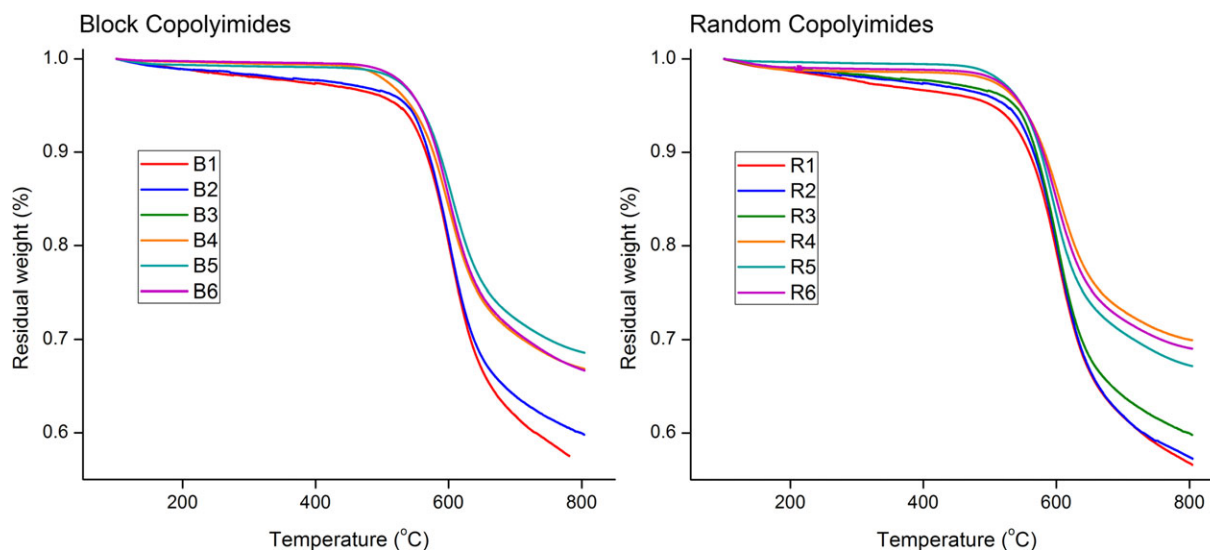


Figure 3. TGA curves of block and random copolyimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Dynamic mechanical analysis is powerful and preferred technique for measuring the T_g , particular for rigid polymer systems. The temperature dependence of the dynamic storage modulus and $\text{Tan } \delta$ of copolyimides are shown in Table IV and Figure 4. The glass transition temperature of films was measured as the peak of the $\text{Tan } \delta$ curve. Random copolyimide showed the T_g in the range of 285–351°C and that of block copolyimide was in the range of 294–377°C. Results indicate that all copolyimides showed higher T_g than that of sBPDA/ODA homopolyimide. T_g increased with increasing the rigid APBI block length and molar ratio. T_g of copolyimide systems is directly related to the chain rigidity and ordering of the structure. Rigidity depends upon the structure of monomers and intermolecular forces. Higher chain rigidity would lead to a higher T_g , providing the lower chain mobility.⁴⁴ Addition of APBI would increase the chain rigidity and therefore increased the potential barrier to rotation, which would result in higher T_g values. $\text{Tan } \delta$ denotes the energy consumed by copolyimides under stress. It is clear from the $\text{Tan } \delta$ curves that there is a

decreasing trend in values of $\text{Tan } \delta$ with increasing the rigid APBI molar ratio in both random and block copolyimides. During glass transition process, segmental moves require overcoming the friction among copolyimide chains. $\text{Tan } \delta$ expresses energy consumption in this process and it is related with overall structure of copolyimide. Copolyimide chains with more rigid segments of APBI are difficult to move, and the friction between them is lower, thus the values of $\text{Tan } \delta$ are also lowered. A high T_g generally maintain mechanical properties like storage modulus, at high temperatures. The storage moduli of copolyimides are quite high which can be attributed to rigid backbone structure of copolyimides. The storage moduli gradually decreased in the temperature range from 50°C to 280–360°C and then considerably dropped in their glass transition temperature range. This drop shifted significantly to a higher temperature with the increase of APBI molar ratio in copolyimides. Storage moduli of block copolyimides were slowly decreased and well maintained before glass transition temperature, as compared to corresponding random copolyimides. This may further indicate the

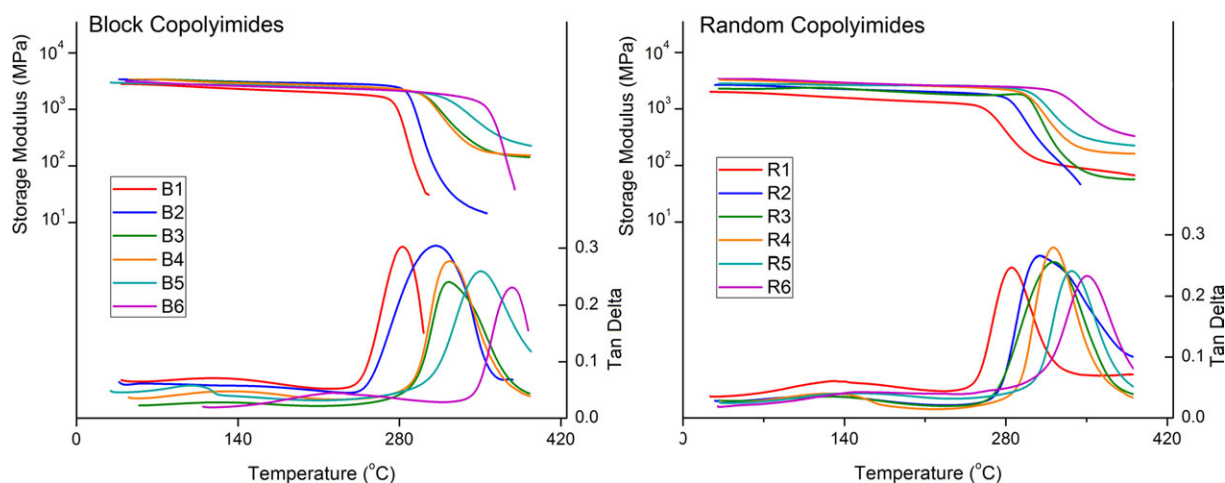


Figure 4. DMA curves of block and random copolyimides. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

existence of highly rigid segmented structure in block copolyimides as argued earlier.⁴⁵ Hydrogen bonding capability of APBI containing the N—H group can be a contributing factor to higher T_g and lower $\tan \delta$ values with increasing the APBI. The hydrogen bonding among polymer chains enhanced the intermolecular interactions. DSC measurement showed similar thermal behavior as in the case of DMA. However, glass transitions were not very well defined in rigid block copolyimide B6.

Mechanical Properties

The mechanical properties of copolyimides are presented in Table V. Random copolyimides exhibited tensile strength of 98–180 MPa, elongation at break of 6.6–9.6% and tensile modulus of 2.8–5.1 GPa. Block copolyimides showed tensile strength of 101–198 MPa, elongation at break of 4.5–7.2% and tensile modulus of 3.0–5.9 GPa. Mechanical properties results indicate that tensile strength and tensile modulus increased linearly with increase in APBI mol %. However, there is an inverse relationship between elongation break and APBI contents in copolyimides. This trend of mechanical properties is more prominent in the case of block copolyimides.

The mechanical properties of the PIs primarily depend upon the chemical structure of the PIs, inherent viscosity, crystallinity, and macromolecular orientation. Generally, PIs with the higher intrinsic viscosity, crystallinity, and macromolecular orientation are supposed to have better mechanical properties. Inherent viscosity increased after PAA formation but only inherent viscosity

Table V. Mechanical Properties of the Random and Block Copolyimides

Sample	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (GPa)
B1	101	7.2	3.0
B2	113	6.9	3.4
B3	128	6.5	3.9
B4	154	6.2	4.3
B5	177	5.7	5.0
B6	198	4.5	5.9
R1	98	9.6	2.8
R2	109	9.2	3.0
R3	122	8.7	3.3
R4	145	8.1	3.7
R5	165	7.6	4.1
R6	180	6.6	5.1

cannot be major factor responsible for improvement in mechanical properties. WAXD was used to illustrate the aggregation state of copolyimides (discussed later). WAXD curves showed that all copolyimides are amorphous in nature. Therefore, it can be said that APBI-based rigid polymer structure plays a major role in the improvement of mechanical properties. Extensive delocalization of π -electrons in PBIs is also well known for their outstanding mechanical properties.

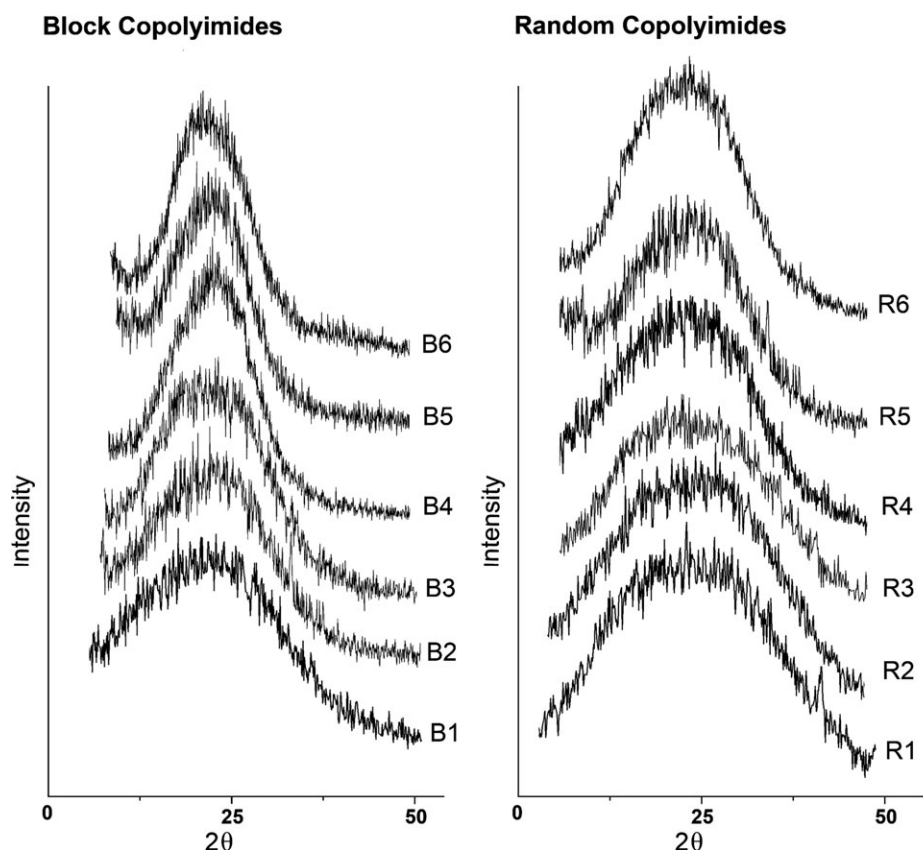


Figure 5. WAXD curves of block and random copolyimides.

In the copolyimides, there is a possibility that N—H groups in imidazole can form hydrogen bonds between the main chains enhancing intermolecular chain interactions. FTIR spectra show a broad N—H stretching band in the region of 3800–3200 cm^{-1} . Intensity of this broad band especially in block copolyimides, increase with increase in APBI molar ratio in copolyimides which indicate the participation of N—H groups of imidazole ring in hydrogen bonding. It seems that hydrogen bonding capable N—H groups in copolyimide blocks are more oriented along block chain length and so, hydrogen bonding appeared more effective in block copolyimides.

WAXD and SEM

The WAXD curves of random and block copolyimides are presented in Figure 5. WAXD curves of all copolyimides exhibited broad diffraction peaks at about $2\theta = 20^\circ\text{--}22^\circ$, which indicates that they are amorphous. However, shape of block copolyimides peaks is narrower than that of random copolyimides. The shape of WAXD curve expresses indirectly the extent of the orientation in the polymers. The narrow shape of peaks shows the higher degree of orientation and ordered structure. This suggests that block copolyimides possess highly oriented and ordered structure as compared to random copolyimides.

SEM photographs of the side views of random and block copolyimides films with higher APBI contents (R4–R6 and B4–B6), are shown in Figure 6. SEM images of block copolyimide films exhibited a densely packed layered pattern, which is parallel to the film axis. It indicates that highly ordered structure of block copolyimides as discussed in CTE discussions. Although random copolyimide lack such definite pattern and showed a roughly smooth surface. This interpretation is also in agreement with WAXD results.

Dielectric Constant and WU

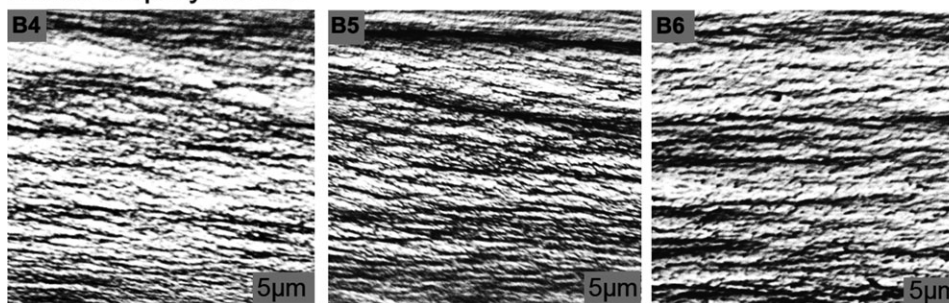
The WU values of all the copolyimides are presented in Table VI and ranged from 1.91 to 2.33. Water absorption behavior of polymers is significantly influenced by concentration of polar groups and their affinity to water molecules. Copolyimides investigated in this study have hydrophilic imidazole N—H groups, which can take water molecules through hydrogen bonding. WU in copolyimides with higher APBI contents exhibited slightly higher water absorption. This can be attributed to higher concentration of hydrophilic imidazole N—H.^{46–50}

Dielectric constants of copolyimides range from 2.67 to 3.05 and relatively lower than those of conventional PIs, but somewhat higher as compared to fluorinated and nanoporous PIs having ultralow dielectric constants.^{51,52} Copolyimides showed a slowly rising trend in dielectric constant with increase in APBI contents. It can be attributed to decreasing free volume with increasing polymer chains packing in higher APBI contents copolyimides.

CONCLUSIONS

Random and block copolyimides with various diamine compositions, were successfully synthesized by thermal imidization and a comparison was made between thermal and mechanical properties of both types of copolyimides. Block copolyimides with variable block lengths were prepared to investigate the effect of block length on properties. The results revealed that introduction of rigid diamine APBI, led to improved thermal and mechanical properties in copolyimides. It enhanced the polymer backbone rigidity and regularity due to its rigid structure and capability to form hydrogen bond. WAXD and SEM studies demonstrated that higher degree of molecular orientation

Block Copolyimides



Random Copolyimides

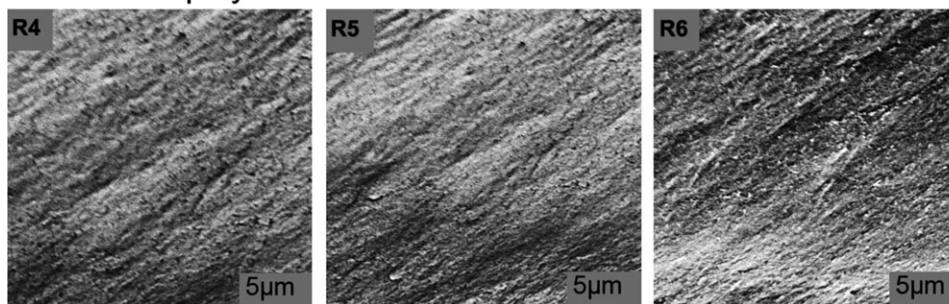


Figure 6. SEM images of block and random copolyimides.

Table VI. Dielectric Constants and Water Uptake of the Random and Block Copolyimides

Sample	Dielectric constant	Water uptake (%)	Sample	Dielectric constant	Water uptake (%)
B1	2.67	1.91	R1	2.70	1.95
B2	2.72	1.98	R2	2.74	2.01
B3	2.82	2.09	R3	2.82	2.11
B4	2.89	2.14	R4	2.90	2.16
B5	2.96	2.23	R5	2.97	2.23
B6	2.99	2.29	R6	3.05	2.33

existed in the amorphous block copolyimides than their random counterparts, and thus, they showed better properties. The results exhibited that increasing the block length of rigid ABPI block improved the properties. Highly oriented block copolyimides showed low CTE, high T_g , better tensile strength, and modulus. All copolyimides showed better dielectric constant and WU than conventional polyimides. Thus, APBI-based block copolyimide systems can be promising candidates for base film materials in microelectronics applications.

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