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Morphological consequences of interchange reactions during solid state copolymerization in poly(ethylene terephthalate) and polycarbonate oligomers

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Abstract

Poly(ethylene terephthalate) (PET) (IV:0.15 dL/g) oligomer was obtained by depolymerisation of high molecular weight PET. Polycarbonate (PC) oligomer (IV: 0.15 dL/g) was synthesized by standard melt polymerization procedure using bisphenol A and diphenyl carbonate in the presence of a basic catalyst. Blends of varying compositions were prepared by melt blending the chemically distinct PET and PC oligomers. The copolymer, poly(ethylene terephthalate-*co*-bisphenol A carbonate) was synthesized by simultaneous solid state polymerization and ester–carbonate interchange reaction between the oligomers of PET and PC. The reaction was carried out under reduced pressure at temperatures below the melting temperature of the blend samples. DSC and WAXS techniques characterized the structure and morphology of the blends, while [1]NMR spectroscopy was used to monitor the progress of interchange reactions between the oligomers. The studies have indicated the amorphisation of the PET and PC crystalline phases in solid state with the progress of solid-state polymerization and interchange reaction.
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1. Introduction

Poly(ethylene terephthalate) (PET) is commercially the most successful member of the thermoplastic polyester family. Some PET applications require modification of the base polymer [1–3]. For example, in blow molding an increase in the glass transition temperature is useful in reducing the crystallization ability and increasing the melt strength. It is relatively less tough and soluble in few solvents such as trifluoroacetic acid (TFA) and *o*-chlorophenol. On the other hand bisphenol A polycarbonate has high impact strength and is soluble in common solvents such as chloroform. A copolymer or a blend made from the two could give a material with combined properties [1–8].

PET/PC blends have been studied extensively and many reports were published in the literature on the miscibility of these blends [1–19]. Paul et al. [9,10] reported that the blends were miscible at higher PET content (above 70%), while others [11,13] found that blends were completely immiscible over all composition range. Wang et al. [1] found that the blend became entirely miscible only after the transesterification reaction between PET and PC. Much of the previous research was focused on preparing the miscible PET/PC blends by reactive blending via transesterification [1,4,5,9,10,15–19]. Transesterification reactions strongly depend on their initial compatibility and on the blending conditions. It is generally accepted that, as a result of transesterification reactions, the blends of homopolymers transform into block copolymers that subsequently transform into a random copolymer as block lengths gradually decrease [20]. Possible reactions in PET/PC blends during melt processing were well documented in the literature [4,21–24].

Most of the transesterification reactions are carried out in the melt state. However, there are few reports describing transesterification reactions in solid state. Nirmala et al., [25] studied the simultaneous solid state and exchange reactions in PET/PEN oligomers. Hait and Sivaram [26,27]

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demonstrated that carbonate–ester interchange reactions could occur along with the solid-state polymerization (SSP) in the case of PET/PC.

The focus of this paper is to examine the structure and morphology development during ester–carbonate interchange reaction and solid state polymerization of PET/PC oligomer blend. The PET/PC oligomers were initially melt blended and crystallized. The crystallized blend was subjected to simultaneous solid state polymerization and ester–carbonate interchange reaction by holding the blend just below the melting temperature under reduced pressure. The change in the structure and morphology was monitored by ^{1}H NMR spectroscopy, DSC and X-ray diffraction.

2. Experimental

2.1. Preparation of oligomers

PET oligomer was prepared by hydrolysis of high molecular weight PET pellets (η_{inh}: 0.69 dL/g) obtained from Eastman Chemicals, USA. Hydrolysis was carried out using deionized water in a Parr reactor at 180 °C for 1.5 h. The oligomer obtained was filtered and dried at 60 °C under reduced pressure. An oligomer of polycarbonate was prepared by melt polymerization of bisphenol A with diphenyl carbonate in the presence of a basic catalyst [28]. The inherent viscosities of the PET and PC oligomers were 0.16 and 0.14 dL/g (in phenol/1,1,2,2-tetrachloroethane), respectively.

2.2. Preparation of oligomer blends

The blends of PET and PC oligomers were prepared in Midi 2000 co-rotating twin-screw extruder from DSM Research (The Netherlands). The batch size was about 5 gm and the oligomers were blended at 250 °C for 1 min, with a screw speed of 100 rpm to minimize the transesterification during blending. For the comparison purpose the PET and PC oligomers were also passed through the twin-screw extruder under similar conditions as in the case with the blend samples before performing SSP.

2.3. Crystallization and solid state polymerization

The PET oligomer crystallized during cooling after extrusion, however, the PC oligomer in the blend was crystallized under chloroform vapors for 4 h at room temperature. The catalyst antimony trioxide (1000 ppm) was incorporated by refluxing the sample in acetone for 1 h. Acetone was stripped off in a rotatory evaporator and the oligomer blend was dried under vacuum at 60 °C. The SSP was performed in a glass reactor according to a well-defined time temperature protocol under reduced vacuum. Samples were periodically removed for structure and morphology characterization.

2.4. Characterization

Inherent viscosities were measured at 30 °C in an automated Schott Gerate AVS 24 viscometer, using an Ubbelohde suspended level viscometer in phenol/1,1,2,2-tetrachloroethane (TCE) (60:40, w/w) at a polymer concentration of 0.5%. The X-ray diffraction experiments were performed using a Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator with a copper target and a wide-angle powder goniometer, having diffracted beam graphite monochromator. The generator was operated at 40 kV and 150 mA. All the experiments were performed in the reflection mode. The samples were scanned between $2\theta = 5$–$35°$ at a speed of $1°$/min. Calorimetric measurements were performed using a Perkin–Elmer thermal analyzer (DSC-7) at a heating/cooling rate of 10 °C/min in a nitrogen environment. ^{1}H NMR was performed in a Bruker DRX 500 spectrometer at 25 °C operating at 500 MHz. The samples were dissolved in $CDCl_3$/TFA (70:30, v/v) mixture and the spectra were internally referenced to tetramethyl silane.

3. Results and discussions

3.1. Solid state polymerization and interchange reaction

Crystallized oligomer blends were subjected to SSP as per the temperature/time protocol shown in Table 1 under dynamic reduced pressure. Fig. 1 shows the change in inherent viscosity (η_{inh}) with time during SSP. The starting SSP temperature is 190 °C and is dictated by the onset of melting of the crystallized sample. In general, PET oligomer displayed a higher onset of melting, but the PC component always showed lower melting temperature necessitating lower SSP temperature. The SSP temperature is progressively increased during the course of the reaction because the onset of melting shifted to higher temperature with increase in the SSP time. All the compositions underwent solid-state polymerization to significant extent as indicated by the increase in inherent viscosity with time. The final viscosity attained by these blend samples differs with composition, even though the SSP time temperature protocol is the same for all samples. Nevertheless it must be kept in mind that the PET, PC and copolymer will have different sets of Mark–Houwink constants for the given polymer-solvent

Table 1
Temperature/time protocol used for SSP

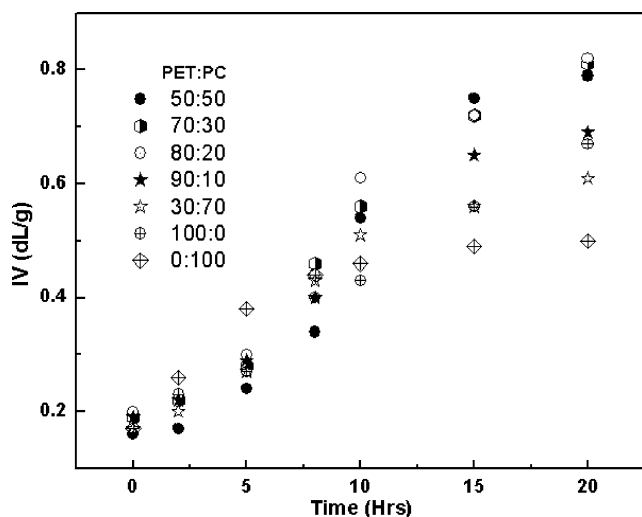| Temperature (°C)	Time (h)
190	1.0
200	1.5
210	2.5
220	3.0
230	12.0

Fig. 1. Change in inherent viscosity (η_{inh}) for PET/PC blend samples of different compositions during SSP.

combination. Hence, direct extrapolation of viscosity to molecular weight and comparison may not be appropriate.

It has been shown that PET and PC undergo interchange reaction in the melt state and hence it is reasonable to expect that PET and PC will undergo interchange reaction also in the solid state, albeit at lower rates. Fig. 2 shows the NMR spectra for 70:30 and 30:70 PET/PC blend samples at various stages of SSP. In PET ^{1}H NMR spectra, 8.02 ppm corresponds to the four protons of terephthalic acid residue. The signals in the 7.00–7.20 ppm region correspond to the

aromatic protons of bisphenol A in PC. Crystallized oligomer blend does not show signals in the range of 8.1–8.4 ppm indicating that no transesterification takes place during melt mixing the oligomers and subsequent crystallization. With progress in SSP, new NMR peaks start to appear at 8.14, 8.20 and 8.30 ppm indicating interchange reaction also occurring simultaneously with chain extension. It may be noted that the region 7.0–7.2 ppm also shows the effect of transestrification, however, the shift is too close for meaningful quantification. On the other hand in the region 8.1–8.4 the peaks are well resolved and used for quantitative analysis. The molecular structure of the copolymer may be analyzed from the NMR data.

The ester–carbonate interchange reaction between PET and PC oligomers leads to the formation of a four-component polycondensate, which can be represented by the general formula

$$-[(A_1-B_1)_x-(A_2-B_1)_y]_m-[(A_1-B_2)_z$$

$$-(A_2-B_2)_w]_n-$$
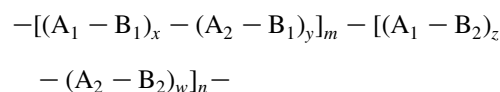
where A_1 is the ethylene group, A_2 is the bisphenol A group, B_1 is the terephthalate unit and B_2 is the carbonate unit. The percentage transesterification and degree of randomness can be calculated from the triad mole fractions obtained from ^{1}H NMR. In term of triads, by considering the terephthalic unit B_1 as the central unit, in the final copolymers three different sequences can be identified as shown in Scheme 1. Depending on the environment, the terephthalic protons in B_1 show signals at 8.14, 8.20 and 8.30 ppm corresponding to
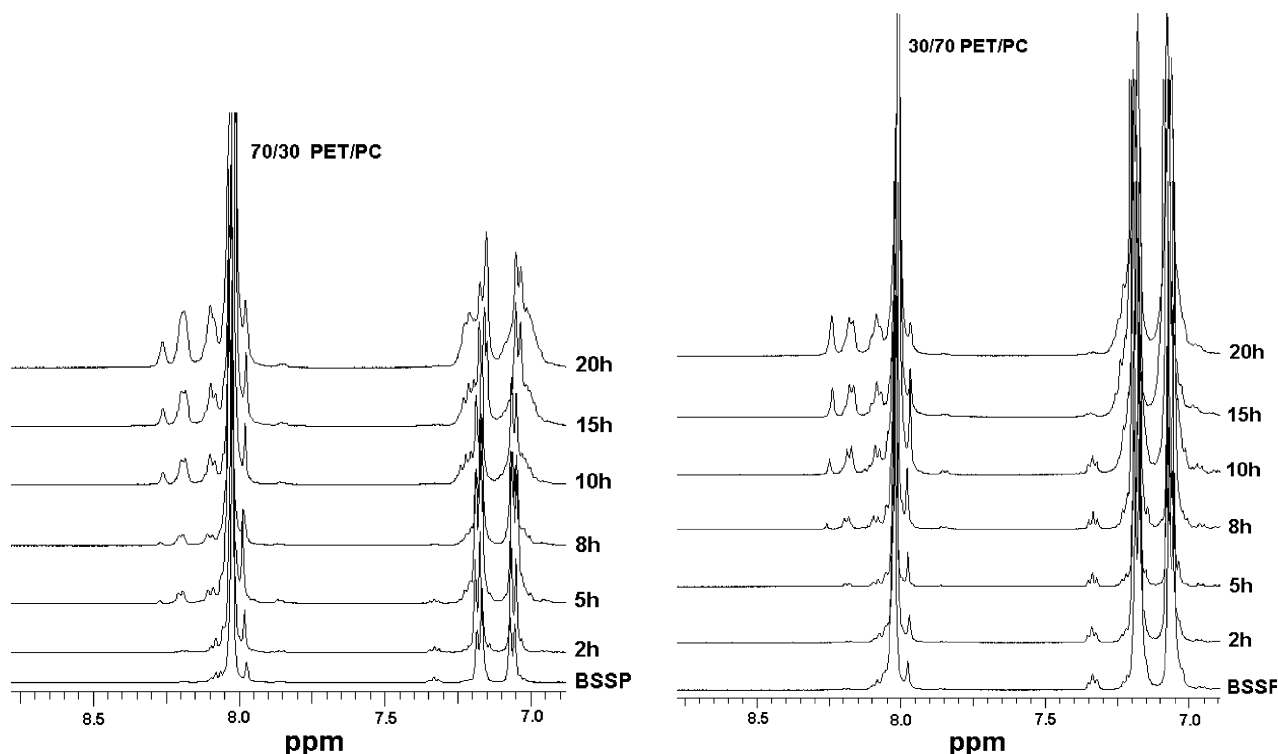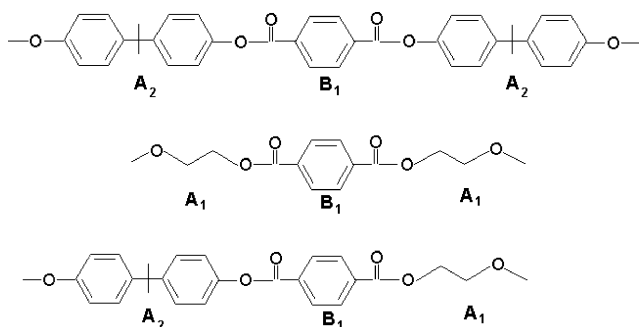

Fig. 2. ^{1}H NMR spectra at various stages of SSP for the compositions PET/PC 70/30 and 30/70.

Scheme 1. Possible triads present in the PET/PC copolymer as terephthalic unit (B_1) as the central unit. A_1 is the ethylene group, A_2 the bisphenol A group.

$A_1B_1A_2$ and $A_2B_1A_2$ triads, respectively. The mole fractions of triads of type $A_iB_1A_k$ relative to the concentration of B_1 [$f(A_iB_1A_k)$] can be obtained directly from the integrated intensities of the appropriate NMR peaks. The degree of randomness (B_{B1}), which is indicative of how the A units are distributed around B_1, can be written as:

$$B_{B1} = f_{A1B1A2}\left(\frac{1}{F_{A1}} + \frac{1}{F_{A2}}\right)$$

where f_{A1B1A2} is the mole fraction of $A_1B_1A_2$ triad, F_{A1} and F_{A2} are the mole fractions of ethylene glycol and bisphenol A, respectively. The f_{A1B1A2} value is calculated from ^{1}H NMR spectra, by measuring the relative intensity of the signals due to the $A_1B_1A_2$ sequence. B_{B1} can assume values between 0 and 2. For random copolyesters B_{B1} is unity and if B_{B1} is less than unity, the units tend to cluster together in blocks of each unit. If B_{B1} is zero it indicates a mixture of homopolymers, whilst a value of 2 indicates an alternating distribution [29].

The degree of transesterification (DT) is

$$\frac{(f_{A1B1A2} + f_{A2B1A2})}{(f_{A1B1A1} + f_{A1B1A2} + f_{A2B1A2})} = f_{A1B1A2} + f_{A2B1A2}$$

where $f_{A1B1A1} + f_{A1B1A2} + f_{A2B1A2} = 1$

The degree of randomness and % of transesterification calculated from the NMR data is shown in Fig. 3. It is apparent from the figure that the transesterification is minimum during the initial hour of reaction and the increase in the viscosity is due to self-condensation of homopolymers. However, transesterification becomes appreciable after 8 h of reaction. The degree of randomness is close to zero initially indicating long sequences of homopolymer blocks. The degree of randomness increases with increase in transesterification indicating the sequence of the blocks becoming shorter. However, degree of randomness is always below unity, indicating the presence of blocks of homopolymer chains. Small peaks at about 4.3 and 6.8 ppm are also observed in the NMR spectra and are assigned to aromatic–aliphatic ether linkage and cyclic ethylene

carbonate. These products arise from the side reactions as discussed in detail by Hait and Sivaram [26].

3.2. Structure and morphology

The change in the WAXS patterns of the 50/50 blend sample during the course of SSP is shown in Fig. 4, as an example. Other compositions also exhibited similar behaviour. The before solid-state polymerization (BSSP) sample shows a prominent peak at $2\theta = 17.32°$ with a shoulder at $2\theta = 16.25°$. PET and PC have major reflections in the 2θ ranges from 14 to 20°. PC shows a major reflection at $2\theta = 17.02°$ corresponding to 210 reflection and the other reflections are relatively weak [30]. In the case of PET, the strong reflections $0\bar{1}1$ and 010 occur at 15.92 and 17.46°, respectively [31]. The other prominent reflections of PET are at $2\theta = 21.16$, 22.36 and 25.73° and are indexed as $\bar{1}11$, $\bar{1}10$ and 100 [31]. In the blend samples, these reflections appear weak. This would imply that the crystallization of PET in the presence of PC is retarded, even though PET has a higher crystallization rate. To understand the crystallization behavior of PET/PC oligomeric blends, PET and PC oligomers were crystallized individually and physical mixtures were prepared in 30/70, 50/50 and 70/30 compositions at room temperature. The diffraction patterns of the mixtures are very similar to those of respective melt blended samples. This indicates that both PET and PC crystallize individually in the melt blended samples as in the case with homopolymers.

The X-ray diffraction patterns show increase in the amorphous content with progress in reaction. All the blend samples show decrease in crystallinity after 5 h of reaction, even though the reaction temperature is below the onset of melting. It is interesting to note that the amorphization starts after 5 h of SSP when the interchange reaction becomes prominent. It must be noted that though the amorphous fraction increased, the diffractograms still exhibited the basic shape of the before SSP diffractogram, indicating the existence of PET and PC crystals in the ASSP sample.

The thermal properties of the samples are studied in detail to understand the structure and morphology. DSC thermograms of the crystallized samples are shown in Fig. 5. The thermograms of PET and PC oligomers are also sketched in the same figure for comparison. As seen from the Fig. 5, the melting temperature of PET is depressed in the blend samples, however, such depression is not obvious for the PC component. The behaviour of the melting endotherms with SSP and interchange reaction is shown in Fig. 6 for the composition 50/50. The PC melting endotherm shifts to higher temperature with increasing reaction time, while the position of PET does not change. During the final stage of the reaction, the thermograms overlap. The heat of fusion is plotted with reaction time in Fig. 7. Table 2 gives heat of fusion with reaction time for different compositions along with homopolymers. During initial stages the heat of fusion increases but after 5 h of reaction it starts decreasing
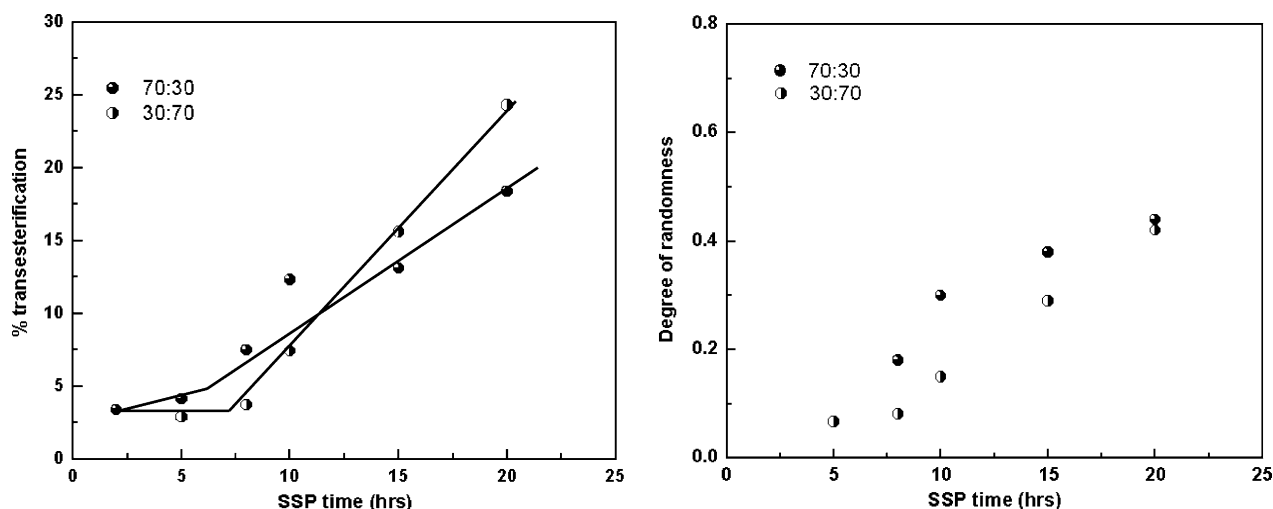
Fig. 3. Degree of randomness and % of transesterification calculated for 70:30 and 30:70 PET/PC blend samples at various stages of SSP from ^{1}H NMR.

indicating amorphization and is consistent with XRD data discussed above. However, under similar conditions the heat of fusion of the homopolymers shows an increase initially but becomes constant at later stages of reaction.

It is worth comparing the behavior of PET–PC system with PET–PEN system. In the case of simultaneous solid state polymerization and exchange reactions of PET/PEN oligomer blends, such amorphization was not observed with the progress of the reaction in the solid state and the PET and PEN crystals remained unchanged [25]. The amorphization in the case of PET/PC may be explained on the basis of co-crystallization. PET and PEN have very similar chemical structure and crystallize in the triclinic structure. It has been shown that PET and PEN can co-crystallize in the same lattice [32,33]. Hence, it appears that in the case of PET–PEN system, the PET and PEN react to form a copolymer. The copolymer stem can be accommodated in the outer layer of the crystals of PET and PEN and this protects the crystal from further reaction. The reaction is not expected to take place within the crystals as these crystals are big and defect free. However, the situation is different for PE–PC system. PET and PC have different chemical structure and they crystallize in different crystal lattices and cannot co-crystallize. When PET–PC copolymer is formed on the outer layer, the stem is rejected from the crystal, thus exposing the inner layer for further reaction. Thus there is continuous reduction in the crystals leading to amorphisation below the melting temperature.

Glass transition temperatures were not observed in the first heating runs for the BSSP sample because the starting sample was partially crystalline. However, glass transition is seen in the after SSP samples probably due to the increased amorphization and Fig. 8 shows the variation of T_g with composition. As expected the T_g's of the samples solid state polymerized for 20 h show a linear relationship with composition and these values agree well with the computed values on the basis of linear relationship between T_g's of the components [34].
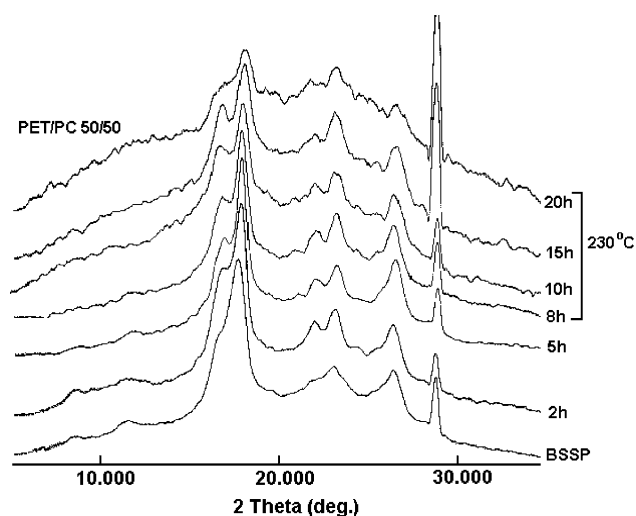

Fig. 4. X-ray diffraction patterns of the 50/50 PET/PC blend sample during the course of SSP. The peak at 28.45° shows the silicon (111) reflection, which is used as the internal standard.
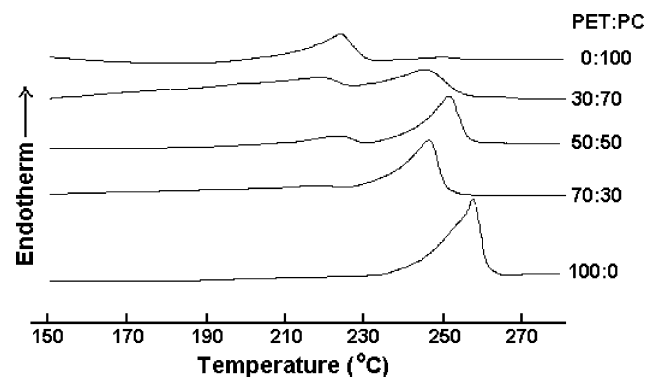

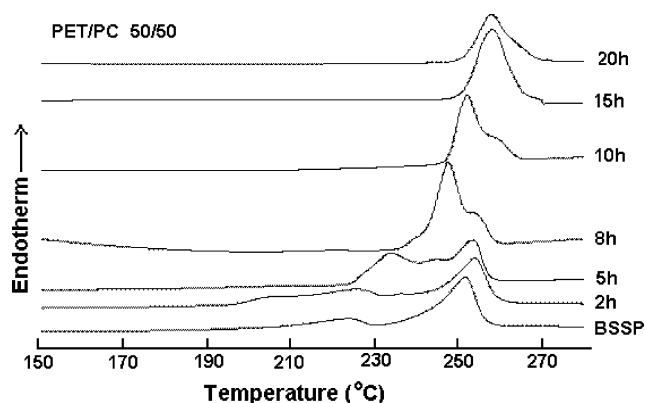Fig. 5. DSC thermograms of the crystallized oligomer samples PET, PC and blends of different compositions.

Fig. 6. The melting behaviour of 50/50 PET/PC blend sample at various stages of SSP.

Fig. 8. Dependence of glass transition temperature on the composition of PC in the copolymers.

The melting endotherms in the first heating are not representative of the copolymer melting because the morphology has individual PET and PC crystals. Hence samples were melted and quenched and again heated in DSC to study its crystallization and melting behaviour. The thermograms are shown in Fig. 9 for the composition 50/50. All the samples showed the effect of transesterification on crystallization and melting. The cold crystallization peaks due to PET (T_c) are evident for these samples. There is an additional crystallization exotherm for PET at higher temperature; however, the amount representing this peak is small. These peaks progressively shift towards higher temperature and become smaller and broader during SSP and transesterification. The heat of fusion and melting temperature also decrease. These suggest that crystallization is hindered due to the disruption of chain periodicity as a consequence of transesterification [35] as well as due to the increase in molecular weight.
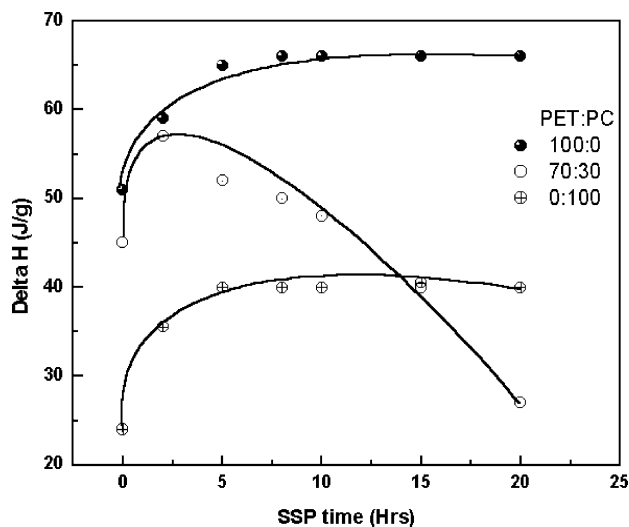
5. Conclusions

Poly(ethylene terephthalate-*co*-bisphenol A carbonate) was obtained by simultaneous solid state polymerization and transesterification of crystallized PET/PC oligomers. The ^{1}H NMR data indicates that interchange reactions are prevalent during later stages of SSP. The degree of randomness increases with increase in transesterification reaction. The ^{1}H NMR results are correlated with thermal and WAXS studies to understand the structure and morphology of the copolymer obtained. DSC and WAXS results reveal the amorphisation of PET and PC crystals below the melting temperature with the progress of SSP and transesterification. DSC studies on the SSP samples showed that, with increase in transesterification and viscosity, the

Fig. 7. Change in heat of fusion of homopolymers PET, PC and 70/30 PET/PC blend at different level of SSP and transesterification.

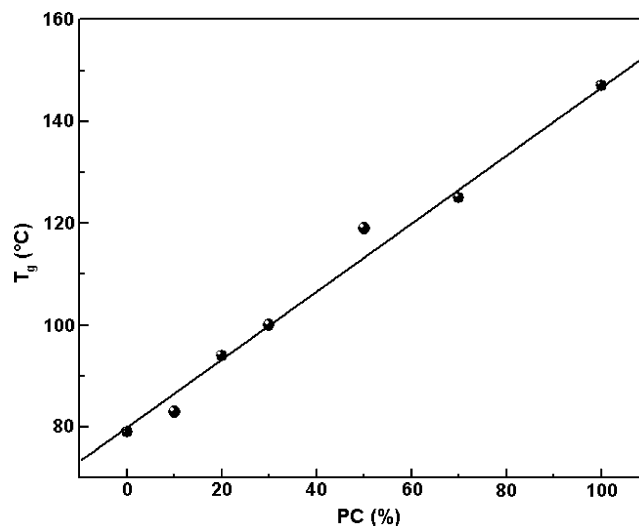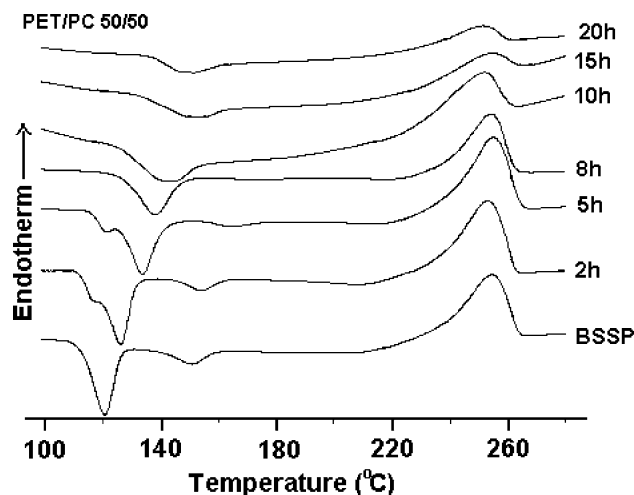Fig. 9. DSC thermograms of PET/PC 50:50 blend sample at different level of SSP and transesterification (Note: samples were rapidly melted and quenched before scanning).

Table 2
Change in heat of fusion for different compositions of PET/PC blends along with homopolymers at different levels of SSP and transesterification

SSP time	Heat of fusion (J/g) (PET: PC)						
	0:100	30:70	50:50	70:30	80:20	90:10	100:0
0	24	37	41	45	47	51	51
2	36	46	57	57	54	58	59
5	40	42	47	52	51	61	65
8	40	40	45	50	53	60	66
10	40	35	40	48	46	54	65
15	41	25	37	40	44	50	66
20	40	21	27	27	32	50	66

crystallization of the copolymers became more and more difficult.

References

[1] Porter RS, Wang LH. Polymer 1992;33:2019.
[2] Porter RS, Jonza JM, Kimura M, Desper CR, George ER. Polym Eng Sci 1989;29:55.
[3] Utaki LA. Polymer alloys and blends. New York: Hanser; 1989.
[4] Pilati F, Marianucci E, Berti C. J Appl Polym Sci 1985;30:1267.
[5] Ignatov VN, Carraro C, Tartari V, Pippa R, Scapin M, Pilati F, et al. Polymer 1997;38:195.
[6] Ignatov VN, Carraro C, Tartari V, Pippa R, Scapin M, Pilati F, et al. Polymer 1997;38:201.
[7] Zheng WG, Wan ZH, Qi ZN, Wang FS. Polym Int 1994;34:301.
[8] Zheng WG, Qi ZN, Wang FS. Polym Int 1994;34:307.
[9] Nassar TR, Paul DR, Barlow JW. J Appl Polym Sci 1979;23:85.
[10] Murff SR, Barlow JW, Paul DR. J Appl Polym Sci 1984;29:3231.
[11] Chen XY, Bireley AW. Br Polym J 1985;17:347.
[12] Hanrahan BD, Angeli SR, Runt J. Polym Bull 1986;15:455.
[13] Suzuki T, Tanaka H, Nishi T. Polymer 1989;30:1287.
[14] Tan Q, Ma DZ. J Appl Polym Sci 1993;48:747.
[15] Zhang GY, Ma JW, Cui BX, Luo XL, Ma DZ. Macromol Chem Phys 2001;202:604.
[16] Marchese P, Celli A, Fioroni M. Macromol Chem Phys 2002;203:695.
[17] Godard P, Dekoninck JM, Devlesaver V, Devaux J. J Polym Sci Part A: Polym Chem 1986;24:3315.
[18] Huang ZH, Wang LH. Makromol Chem Rapid Commun 1986;7:255.
[19] Kong Y, Hay JN. Polymer 2002;43:1805.
[20] Fiorini M, Pilati F, Berti C, Toselli M, Ignatov V. Polymer 1997;38:413.
[21] Licciardello A, Auditore A, Samperi F, Puglisi C. Appl Surf Sci 2003;203/204:556–60.
[22] Godard P, Dekoninck JM, Devlesaver V, Devaux J. J Polym Sci Part A: Polym Chem 1986;24:3301.
[23] Eguiazabal JI, Ucar G, Cortazar M, Iruin JJ. Polymer 1986;27:2013.
[24] Berti C, Bonara V, Pilati F. Makromol Chem 1992;193:1665.
[25] James NR, Ramesh C, Sivaram S. Macromol Chem Phys 2001;202:2267.
[26] Hait SB, Sivaram S. Macromol Chem Phys 1998;199:2689.
[27] Hait SB, Sivaram S. US 6150493; 2000.
[28] Iyer VS. PhD Thesis, University of Poona; 1994.
[29] Yamadera R, Murano M. J Polym Sci A 1967;5:2259.
[30] Radhakrishnan S, Iyer VS, Sivaram S. Polymer 1994;35:3789.
[31] Murthy NS, Correale ST, Minor H. Macromolecules 1991;24:1185.
[32] Wendling J, Suter UW. Macromolecules 1998;31:2516.
[33] Lu X, Windle AH. Polymer 1995;36:451.
[34] Sperling LH. Introduction to physical polymer science. New York: Wiley; 1992.
[35] Lee SC, Yoon KH, Park IIH, Kim HC, Son TW. Polymer 1997;38:4831.