

Polymer Communication

Liquid induced crystallization of poly(ethylene naphthalate) oligomers

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Abstract

Amorphous poly(ethylene naphthalate) (PEN) oligomer has been crystallized at room temperature by treating in liquids having solubility parameter, δ , in the range of 15–29 (J cm^{-3})^{1/2}. It has been observed that the liquids having δ in the range of 18.5–25 are able to crystallize PEN oligomer efficiently. A direct correlation has been observed between δ and crystallite size calculated from WAXS technique. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Crystallization; Poly(ethylene naphthalate); Solubility parameter

1. Introduction

It is known that in the presence of certain interactive liquids, crystallization of amorphous polymers can occur at room temperature well below the glass transition temperature of the polymer. The liquid induced crystallization in PET has been studied in detail [1–4]. There are a few reports regarding liquid induced crystallization of high molecular weight PEN. The liquids mainly studied are dioxane, aniline, DMF and methylene chloride whose solubility parameters, δ , are 20.42, 22.6–24.2, 24.9, 19.9 (J cm^{-3})^{1/2}, respectively. Solubility parameter of PEN is 20.31 (J cm^{-3})^{1/2} (calculated by Synthia method) [5]. Kim et al. reported [6] that the samples treated in dioxane above 40°C exhibited α -crystalline form and a spherulitic texture, while crystallization at 25°C gave β -crystalline form and an amoebae structure. DMF treated samples mainly showed α -crystalline form irrespective of the treatment temperature. But a trace of β -crystalline structure was observed in the sample treated at 10°C. The β -crystal occurred at lower treatment temperature in liquid induced crystallization while it occurred at higher crystallization temperatures in the case of thermal crystallization [7,8]. PEN could be crystallized in the presence of ethylene glycol or water under pressure at temperatures of 170 and 160°C [9]. Crystallization in this process cannot be treated as liquid induced as the solubility parameter of ethylene glycol is 29.1–33.4 and that of water is 48.

In the present work, PEN oligomer is crystallized by

liquids having a wide range of solubility parameters and the role of solubility parameter on crystallization is studied. The liquids used are diethylether (15.2–15.6), carbon tetrachloride (17.7), ethylacetate (18.6), toluene (18.2–18.3), benzene (18.5–18.8), chloroform (18.9–19), dichloromethane (19.9), acetone (20–20.5), ethanol (26.0–26.5) and methanol (29.2–29.7). There has been no prior report on liquid induced crystallization of PEN oligomers.

2. Experimental

2.1. Preparation of oligomers

The PEN oligomer was prepared by disproportionation of high molecular weight PEN. The PEN pellets and excess of ethylene glycol were taken in 1000 ml round bottom flask. The temperature was raised to 190°C while the pellets were stirred thoroughly. The reaction was continued for 10 h. The residue was filtered and washed with hot water and methanol and dried at 80°C for 12 h. The inherent viscosity of the sample was 0.18 dL g⁻¹ and was measured at 25°C in automated Schott Gerate viscometer using Ubbelohde suspended level viscometer in 40/60 (w/w), phenol/1,1',2,2'-tetrachloroethane solvent mixture at a concentration of 0.5%. The oligomers were melted and quenched in liquid nitrogen to obtain amorphous materials. The DSC thermogram of these samples confirmed the amorphous nature.

2.2. Crystallization

The samples were crystallized at room temperature by stirring the oligomer in the liquids for about 12 h. Samples

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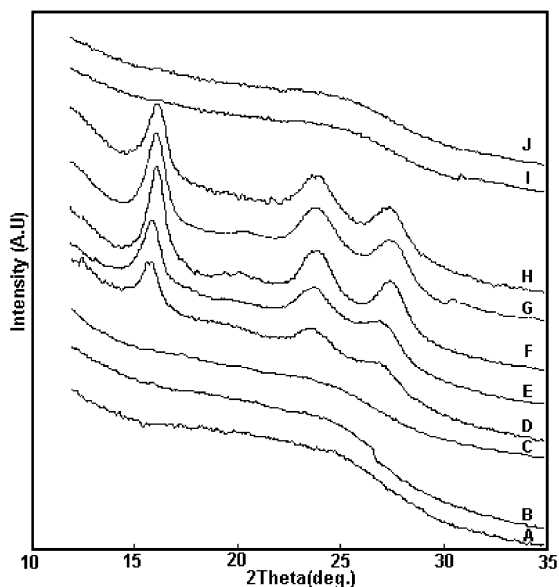


Fig. 1. XRD patterns of PEN oligomer after liquid induced crystallization: (A) diethylether, (B) carbon tetrachloride, (C) toluene (D) benzene, (E) ethylacetate, (F) chloroform, (G) dichloromethane, (H) acetone, (I) ethanol and (J) methanol.

were removed by filtration and dried under reduced pressure at 50°C. The oligomer sample was also melt crystallized at 200°C.

The WAXS pattern of the crystallized samples was obtained in reflection mode using a Rigaku Dmax 2500 diffractometer and Ni filtered copper radiation. The sample was scanned in the range $2\theta = 10\text{--}35^\circ$ and the generator was operated at 40 kV and 150 mA. The FWHM of the $\bar{1}10$ peak was determined by peakfitting software available with the Rigaku diffractometer. The apparent crystal size was calculated from FWHM using Scherrer equation. The calorimetric measurements were done using Perkin–Elmer DSC-7. The samples were heated at a rate of 10°C/min under nitrogen environment.

3. Results and discussion

The X-ray diffraction patterns of the oligomer PEN

Table 1
Crystallization of PEN by liquids

Liquid	δ (J cm^{-3}) ^{1/2}	Crystal size (nm)	Heat of fusion (J/g)	T_m (°C)
Diethylether	15.2–15.6	Amorphous	–	–
Carbon tetrachloride	17.7	Amorphous	–	–
Toluene	18.2–18.3	Amorphous	–	–
Benzene	18.5–18.8	4.7	60	267
Ethylacetate	18.6	4.9	55	270
Chloroform	18.9–19.0	5.2	–	–
Dichloromethane	19.9	5.4	63	270
Acetone	20.0–20.5	5.9	61	269
Ethanol	26.0–26.5	Amorphous	–	–
Methanol	29.2–29.7	Amorphous	–	–

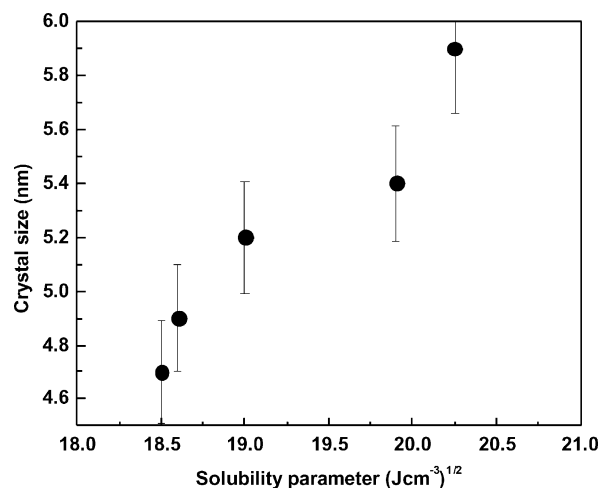


Fig. 2. The apparent crystallite size calculated from the $\bar{1}10$ reflection of PEN is plotted as a function of solubility parameter.

sample crystallized in various liquids are shown in Fig. 1. It is seen from the diffractograms that the diethylether, carbon tetrachloride, ethylacetate, ethanol, toluene and methanol do not induce any crystallinity in the sample and show only the broad peak due to the amorphous phase. On the other hand, the samples treated in liquids benzene, chloroform, dichloromethane and acetone show crystalline peaks at $2\theta = 15.6, 23.3$ and 27.0 indicating that the samples are semicrystalline. These peak positions correspond to the 010, 100 and $\bar{1}10$ diffraction planes of the α -modification. The liquid and its δ value along with the crystal size, heat of fusion and melting temperatures are given in Table 1. It is apparent from the above results that the liquids having solubility parameter in the range 18.5–20.5 are capable of crystallizing PEN. It was earlier shown that liquids having δ values between 20 and 25 can induce crystallinity at room temperature [3]. On the other hand the ethanol and methanol have δ beyond 25 and could not crystallize PEN. From these it may be said that liquids having δ value in the range 18.5–25 are suitable for inducing crystallinity in PEN at room temperature.

In general, the crystalline peaks become sharper when the solubility parameter approaches that of PEN. In Fig. 2, the

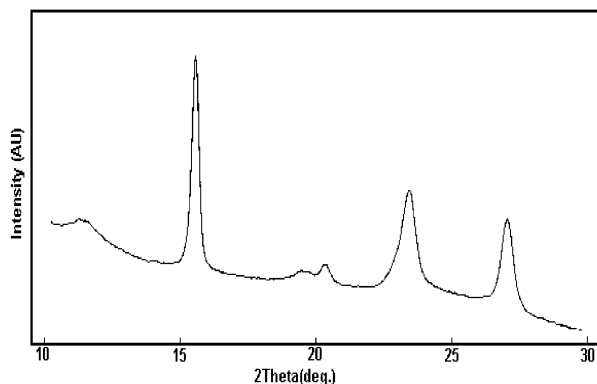


Fig. 3. XRD pattern of PEN oligomer melt crystallized at 200°C.

crystallite size calculated from the reflection $\bar{1}10$ is plotted against the solubility parameter and shows a linear correlation between apparent crystal size and the solubility parameter. It can be seen that as the δ values of the liquids approach that of the polymer, the crystal size shows an increasing trend indicating more compatibility between the liquid and the polymer and hence greater ease of crystallization, resulting in bigger crystallites. However, these samples do not show any variation in melting behaviour. All the samples melt at $\sim 269^\circ\text{C}$ and the heat of fusion is $\sim 60 \text{ J g}^{-1}$. Kim et al. [3] reported that the high molecular weight sample crystallized above 40°C in dioxane showed α -form while at 25°C displayed β -form and attributed the different structures to the difference in the nature of diffusion conditions. In the present case, the XRD patterns showed that all the samples have been crystallized in the α -form, even though the samples are crystallized at room temperature.

It is of interest to compare the diffraction patterns of the liquid induced crystallized samples to that of the samples subjected to thermal crystallization. Fig. 3 shows the WAXS pattern of thermally crystallized sample at 200°C . Very

sharp diffraction peaks and crystallite size of about 15 nm characterize the thermally crystallized oligomer samples [10]. The thermal crystallization behaviour of PEN oligomers have been discussed in detail elsewhere [10]. On the other hand, the samples crystallized by liquids have very broad and less developed peaks in XRD patterns indicating small crystallites compare to thermally crystallized samples. Rebenfeld et al. [11] also made similar observation in the case of PET crystallized in dioxane and aniline and by Makarewicz and Wilkes for PEN [12]. This was attributed to rather small sized yet profuse crystallites induced by the liquid treatments.

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