Synthesis of ultra-high molecular weight poly(ethylene terephthalate) by swollen-state polymerization

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A new polymerization technique for ultra-high molecular weight poly(ethylene terephthalate) (UHMW-PET) has been developed. UHMW-PET was obtained by swollen-state polymerization in specific solvents under bubbling nitrogen gas at atmospheric pressure. Suitable solvents for the swollen-state polymerization were those that could swell PET but did not dissolve it. Solvents having a similar solubility parameter to PET were desirable for attaining higher ultimate intrinsic viscosity at the same polymerization temperature. The rate of swollen-state polymerization was strongly related to the degree of swelling, that is, the content of impregnated solvent in swollen PET. When a hydrogenated terphenyl was used as the solvent, UHMW-PET with an intrinsic viscosity of 2–3 dl g^{-1} was obtained, and a honeycomb-like structure was observed in the UHMW-PET particles.

(Keywords: poly(ethylene terephthalate); polymerization; ultra-high molecular weight)

INTRODUCTION

Some mechanical properties of polymers are strongly related to the molecular weight of the polymer. Mark[1] described that a degree of polymerization greater than 600 was necessary for the desired mechanical properties. Super-high-tenacity fibre is obtained from ultra-high molecular weight polyethylene. Similar results are expected for other conventional polymers and many attempts have been made to prepare polymers having ultra-high molecular weight.

Poly(ethylene terephthalate) (PET) is one of the most widely used plastics and is used in the form of fibres, films, as bottles for beverages, etc. PET is usually obtained by the condensation reaction of bis(2-hydroxyethyl)terephthalate or oligomers at elevated temperature under reduced pressure. This condensation reaction is virtually reversible[2], hence unless glycol, which forms as a by-product, is removed, polymerization does not proceed. Schultz[3] reported that the polymerization rate is related to the concentration of glycol by-product remaining in the polyester, and an effective method for expelling this glycol is necessary for the synthesis of PET. Therefore, it is clear that the effective removal of the by-product is important for obtaining ultra-high molecular weight (UHMW) PET.

Several methods for expelling glycol have been reported[4–8] and UHMW-PET with an intrinsic viscosity of 2 dl g^{-1} was obtained by special solid-state polymerization[9,10]. However, it was difficult to obtain such UHMW-PET by conventional melt polymerization. In melt polymerization, propagation and thermal degradation occur. Tomita[11] showed that with increasing polymerization temperature, the optimum reaction time and the maximum molecular weight are both reduced. Thus polymerization at low temperature is desirable to obtain higher molecular weight PET. However, the polymerization rate at low temperature is slower. Therefore a rapid polymerization method at a low temperature is required for obtaining UHMW-PET.

We have studied the polymerization of PET in the swollen state[12,13]. In this method, the glycol by-product is transferred from the swollen polymer to the solvent and is expelled by bubbling inert gas. This paper describes the swollen-state polymerization in detail.

EXPERIMENTAL

Reagents

PET samples with intrinsic viscosities of 0.6 and 0.35 dl g^{-1} were obtained by conventional melt polymerization from purified terephthalic acid (Mizushima Aroma Co. Ltd) and ethylene glycol. The PET samples were used after granulating to 1–2 mm in diameter.

Solvents

Biphenyl/diphenylether (26:74) mixture (Therm S-300™), monoethylbiphenyl (Therm S-600™), diethylbiphenyl (Therm S-700™) and triethylbiphenyl (Therm S-800™) were obtained commercially as heat transfer media (Nippon Steel Chemical Co. Ltd). These were the isomer mixture. Hydrogenated terphenyl (Therm S-900™) was also obtained commercially (Nippon

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Steel Chemical Co. Ltd). The major component of hydrogenated terphenyl was the mixture of cyclohexylbiphenyl isomers and dicyclohexylbenzene isomers. Diphenylmethane, 1,2-diphenylethane and liquid paraffin were commercial reagents (Nakarai Tesque Co. Ltd). Cyclohexylbenzene and dimethylnaphthalene (mixture of isomers) were also obtained commercially as reagent grade (Aldrich Chemical Co. Inc.). Solvents were purified by distillation before use.

Swollen-state polymerization

Into a glass reactor equipped with a stirrer, a nitrogen gas inlet and a waste gas outlet, were charged 50 g granular PET and 500 ml solvent. The mixture was heated with stirring at 205–237°C under 2–3 l min^{-1} of dry nitrogen gas bubbling through porous glass tube for a period of 2–12 h. Fresh solvent was added constantly to maintain the total volume of reaction mixture. The reaction was continued at the same temperature for 12 h and then allowed to cool. The granular PET was removed, washed thoroughly with acetone and then dried at 130°C under reduced pressure.

Characterization

Intrinsic viscosity of the polymer was measured in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40) at 30°C. Thermal properties of polymers were evaluated by differential scanning calorimetry (d.s.c.; TA-50, Shimazu Co. Ltd) with a heating rate of 20°C min^{-1} under argon atmosphere. The solvent content (degree of swelling) in PET granules was determined by the difference in weight before and after acetone washing. The crystallinity was calculated from the density measured on a density gradient[14].

RESULTS AND DISCUSSION

Effects of solvent

Compatibilities of solvents and PET are estimated by solubility parameters, ∂. Solvents having similar solubility parameters with PET are highly compatible with PET. *Table 1* shows the solubility parameters of solvents calculated by Van Krevelen's method[15]. The solubility parameter of hydrogenated terphenyl was calculated as 4-cyclohexylbiphenyl. Ethyl-substituted biphenyl was also calculated as the corresponding derivatives shown in *Table 1*. It was reported[16] that the experimental value of ∂ for PET was 19.9–21.9 $\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$. The solubility parameter may be divided into three components: ∂d, contribution of dispersion force; ∂p, contribution of polar forces; and ∂h, contribution of hydrogen-bonding component. Solvents with ∂h are known to have a high solubility for PET.

Table 1 Calculated solubility parameters of various solvents

Solvent	Solubility parameter[a] ($\mathrm{J}^{1/2}\,\mathrm{cm}^{-3/2}$) ∂d	∂p	∂h	∂
Phenol	18.68	5.83	15.09	24.71
Benzyl alcohol	18.54	4.97	13.93	23.72
m-Cresol	18.16	4.89	13.83	23.35
Diphenylether	21.48	3.11	4.67	22.20
Biphenyl	22.12	1.20	0	22.15
1,1,2,2-Tetrachloroethane	18.68	10.49	3.91	21.78
(PET)	18.09	4.90	9.89	21.18
1,2-Diphenylethane	19.85	0.96	0	19.88
4-Ethylbiphenyl	20.51	0.94	0	20.53
4-Cyclohexylbiphenyl	19.80	0.71	0	19.82
4,4′-Diethylbiphenyl	19.47	0.77	0	19.49
Cyclohexylbenzene	19.46	0.70	0	19.47
2,5,4′-Triethylbiphenyl	19.16	0.65	0	19.18
n-Decane	16.93	0	0	16.93

[a] ∂d, Component from dispersion forces; ∂p, component from polar forces; ∂h, component from hydrogen bonding; ∂, total solubility parameter of each component

In order to polymerize in the swollen state, the solvents are required to swell PET but not to dissolve PET. Furthermore, solvents for swollen-state polymerization must be thermally stable at the polymerization temperature, that is, they must have high boiling and decomposition temperatures. For these reasons, biphenyl/diphenylether mixture, monoethylbiphenyl, diethylbiphenyl, triethylbiphenyl and hydrogenated terphenyl were selected. These solvents are known as heat transfer media. Other solvents, such as diphenylmethane, 1,2-diphenylethane and dimethylnaphthalene, dissolved PET at the polymerization temperature. On the other hand, although liquid paraffin did not dissolve PET, it scarcely swelled PET. Therefore these solvents were not suitable for swollen-state polymerization.

Figure 1 shows a typical phase diagram of a PET–solvent system. Solvents with a solubility parameter greater than 21 dissolved PET at 235°C. However, solvents with a solubility parameter less than 21 did not dissolve PET and phase separated, molten polymer–solvent formed above 235°C. Every solvent has a swollen state between hard solid and solution.

In the molten state, PET dispersed to form molten droplets above 240°C. By bubbling nitrogen gas, polymerization proceeded in the solvent system; polymer adhered to the wall of the reactor and was hard to remove. However, below 240°C, swollen-state polymerization proceeded in the solvent–PET particle dispersion system.

Effect of polymerization temperature

Using granular PET with an intrinsic viscosity of 0.35 dl g^{-1} as starting material, swollen-state polymerization was carried out in the solvents at various reaction temperatures. At 240–250°C, PET particles coagulated

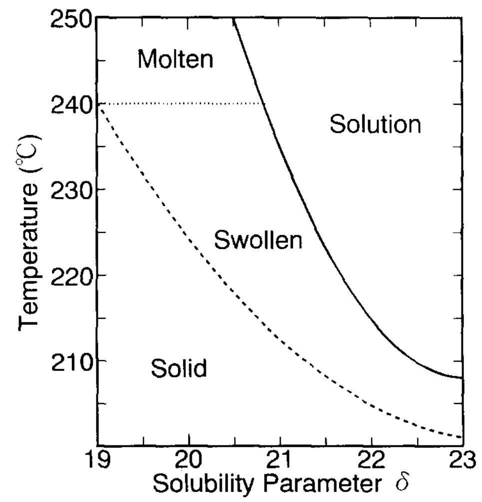

Figure 1 Typical phase diagram of PET–solvent system

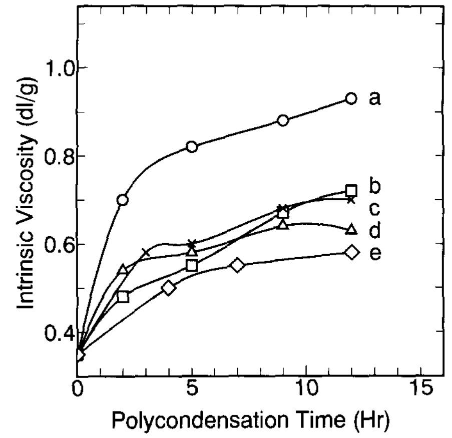

Figure 2 Solvent effect in swollen-state polymerization at 205°C. a, Biphenyl/diphenyl mixture; b, cyclohexylbenzene; c, diethylbiphenyl; d, triethylbiphenyl; e, hydrogenated terphenyl

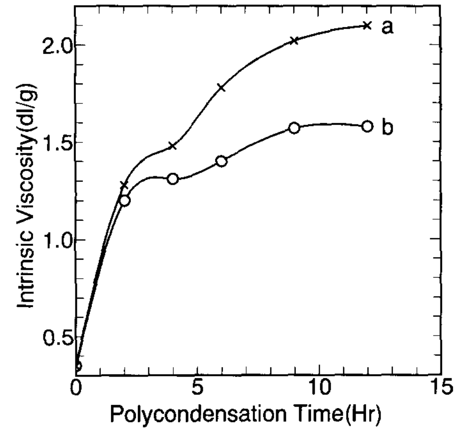

Figure 3 Solvent effect in swollen-state polymerization at 237°C. a, Hydrogenated terphenyl; b, triethylbiphenyl

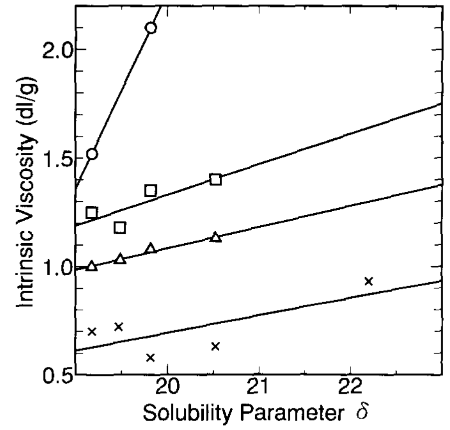

Figure 4 Intrinsic viscosity as a function of solubility parameter ∂ at various temperatures: ○, 237°C; □, 225°C; Δ, 215°C; ×, 205°C

and it was impossible to stir the mixture. The time dependence of intrinsic viscosity was investigated in various solvents at 205 and 237°C, as shown in *Figures 2* and *3*. At 205°C, the preferred solvent was biphenyl/diphenylether mixture, but at 237°C it was hydrogenated terphenyl. In the latter case, PET with an intrinsic viscosity of 2.1 dl g^{-1} was obtained.

Figure 4 shows the relation between intrinsic viscosity and solubility parameter in swollen-state polymerization at various temperatures. The solubility parameter of biphenyl/diphenylether mixture is 22.2, calculated by Van Krevelen's method; this mixture dissolved PET above 215°C, therefore this solvent was not suitable for swollen-state polymerization. The above results also imply that the degree of swelling influences the polymerization rate. The degree of swelling is proportional to the amount of solvent in the polymer and is dependent on the pretreating temperature and time. The content of hydrogenated terphenyl in PET was varied by altering the pretreating time (2–16 h) of PET at 220°C. *Figure 5* shows the relation between the content of hydrogenated terphenyl in the final product (after 12 h polymerization) and the ultimate intinsic viscosity. It is apparent that PET with a higher solvent content could be obtained the higher the ultimate intrinsic viscosity. That is, a solvent that can swell PET penetrates into the polymer, enhancing the mobility of the polymer chain and enlarging the surface area of PET particles. It is presumed that these effects accelerate the removal of glycol by-product from the reaction site and increase the polymerization rate of the chain ends. This penetration of solvent into the polymer formed the unique structure of PET. The scanning electron micrograph (*Figure 6*) shows the fine porous structure of PET obtained from swollen-state polymerization in hydrogenated terphenyl.

The UHMW-PET obtained from swollen-state polymerization possesses a high melting temperature. The d.s.c. profile (*Figure 7*) of UHMW-PET with an intrinsic viscosity of 2.4 dl g^{-1} showed no peak of crystallization on heating, that is, the UHMW-PET was already crystallized during the swollen-state polymerization. The crystallinity of this UHMW-PET was 85.4% calculated from density. The relation between intrinsic viscosity and melting temperature of this product is shown in *Figure 8*. The melting temperature gradually increased with intrinsic viscosity, levelling off at an intrinsic viscosity of 1.5 dl g^{-1}. This implies that increased mobility of the polymer chain in the swollen state enhances the rate of polymerization and simultaneously accelerates the crystallization of PET. Therefore if the crystallization of PET in the swollen state were to be suppressed by any method, UHMW-PET with a higher molecular weight would be obtained. In conclusion, the penetration of solvents into polymer must have played a significant role in the swollen-state polymerization.

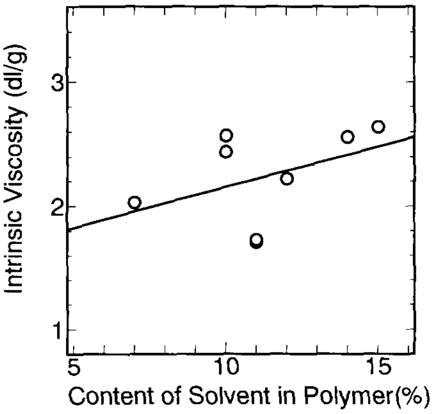

Figure 5 Relation between intrinsic viscosity and degree of swelling (solvent content)

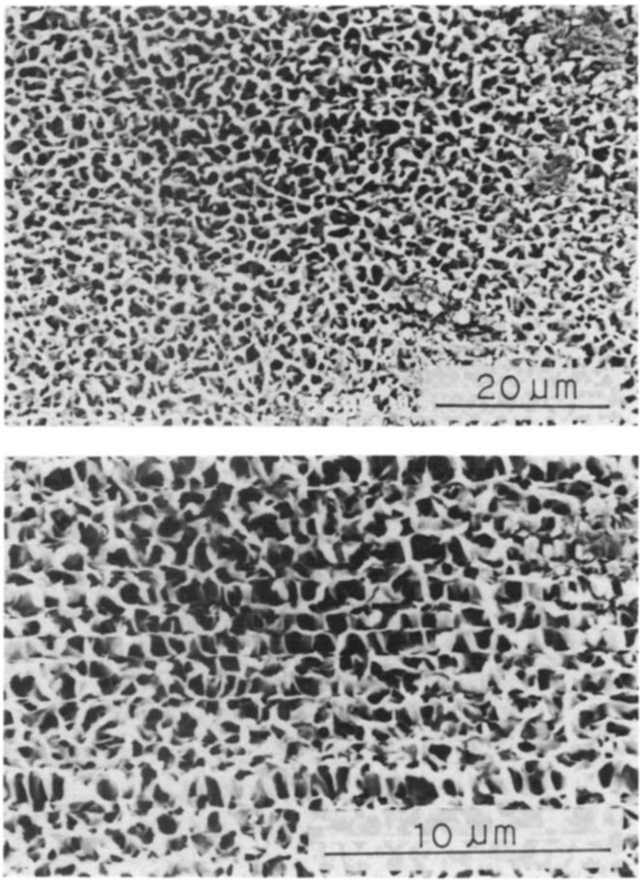

Figure 6 Scanning electron micrographs of the fractured surface of UHMW-PET obtained from swollen-state polymerization

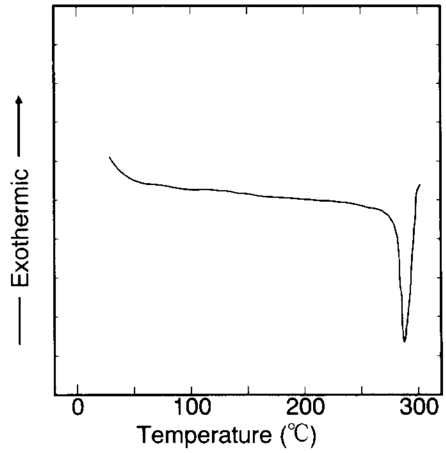

Figure 7 D.s.c. profile of UHMW-PET obtained from swollen-state polymerization. Intrinsic viscosity is 2.4 dl g^{-1}

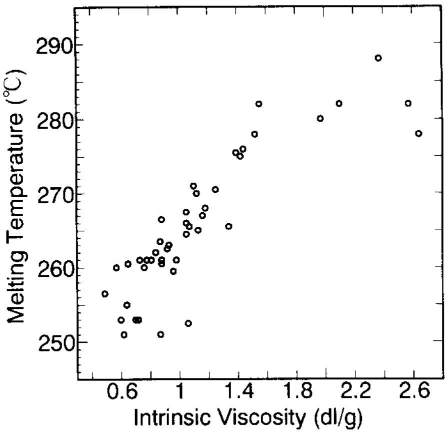

Figure 8 Relation between intrinsic viscosity and melting temperature of PET obtained from swollen-state polymerization

CONCLUSION

The swollen-state polymerization of PET was carried out in specific solvents under bubbling nitrogen gas at atmospheric pressure. The solvents were selected for their thermal and chemical stability. Suitable solvents for swollen-state polymerization were those that did not dissolve PET but could swell it, for example, monoethylbiphenyl, diethylbiphenyl, triethylbiphenyl and hydrogenated terphenyl. Consequently, the rate of swollen-state polymerization was affected by the degree of swelling. The best solvent found for UHMW-PET was a hydrogenated terphenyl, and UHMW-PET with an intrinsic viscosity of 2–3 dl g^{-1} was obtained. The swollen-state polymerization proceeded accompanied by crystallization of PET, and a honeycomb-like structure of UHMW-PET was observed by scanning electron microscopy.

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