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Preparation and characterization of poly(2,6-dimethyl-1,4-phenylene oxide) and Nylon 6 graft copolymer

1. Anionic graft copolymerization of ε-caprolactam on poly(2,6-dimethyl-1,4-phenylene oxide) macroinitiator containing carbonylcaprolactam groups

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SUMMARY

A poly(2,6-dimethyl-1,4-phenylene oxide) (PPO, **1**) macroinitiator having carbonylcaprolactam groups was prepared through metalation of methyl group of PPO and subsequent modification to introduce carboxyl group, acid chloride group, and finally carbonylcaprolactam group. Anionic ring opening copolymerization of ε-caprolactam took place onto the macroinitiator to give a graft copolymer of PPO and Nylon 6. The structure of intermediate materials and the graft copolymer were characterized by ^{1}H NMR, ^{13}C NMR, and IR spectroscopy. Glass transition temperatures and melting temperatures of these materials are also reported. It is found that the copolymer has a micophase-separated morphology even with segment molecular weight as low as 3000.

INTRODUCTION

Since the commercialization of PPO blends, the block and graft copolymers of PPO have received much interest both from the applied and fundamental point of view. These copolymers may act as compatibilizers for the immiscible polymers. PPO/Nylon blends have been developed very recently, and become one of the most important PPO blends because of their balanced mechanical properties. However, only a few studies have been reported on the syntheses of PPO/Nylon copolymers (1,2).

The mechanism of the anionic polymerization of ε-caprolactam is well documented (3~5). The key to initiation and propagation of the linear chain is the formation of the reactive imide group (e.g., N-acyllactam). If a polymer has one of those functional groups along its chain, it may act as a macroinitiator for the anionic caprolactam polymerization.

The chemical modification of PPO may be classified into three categories (6): electrophilic substitution of phenyl ring, metalation of the methyl side chain, and radical attack on the benzylic proton. Among these, metalation of PPO, which was first developed by Chalk and Hay (7), has attracted most attention because various kinds of functional groups can be introduced by further reaction. In this study, the metalated PPO is used as an intermediate material for further modification. By a series of reactions, carboxyl groups, acid chloride groups, and carbonylcaprolactam groups were introduced successively. The final product may serve as an initiator for the anionic polymerization of ε-caprolactam.

The present paper deals with the preparation and characterization of a graft copolymer of PPO and Nylon 6 prepared by anionic polymerization using a PPO macroinitiator.

EXPERIMENTAL

Materials

Commercial PPO was used in this study. The $\overline{M}_w$ and $\overline{M}_w / \overline{M}_n$ as determined from light scattering and GPC are 21600 and 2.2 respectively. It was purified by precipitation with methanol from chloroform solution, and dried in vacuum oven at 70 °C for 48 h. Reagent grade caprolactam was purchased from Sigma Co. and purified by the method described elsewhere (8). N-butyllithium in hexane (2.5 M) was purchased from Aldrich Co. and used as received. All the other reagents and solvents were purified suitable to an anionic polymerization.

Synthesis of ω-Benzyl Ether of Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-BE, **2**)

24 g of PPO ($\overline{M}_n$ = 9800, 2.4 × 10^{-3} mol of -OH) was dissolved in a mixture of 250 ml of distilled toluene and THF (1/1 by volume). 3.3 g of benzylchloride (0.026 mol) and 8.0 ml of 3 N NaOH were charged to the polymer solution, and argon was bubbled for an hour. Finally 0.82 g of tetrabutylammonium hydrogen sulfate (TBAH, 2.4×10^{-3} mol) was added, and the reaction mixture was vigorously stirred for 6 hours at room temperature and then acidified with dilute HCl. The organic phase was separated and precipitated with an excess of methanol. The obtained PPO-BE was filtered and dried in vacuo. Quantitative analysis of the end-capping of PPO was demonstrated by a combination of UV, IR, and NMR techniques.

Preparation of N-(trimethylsilyl)caprolactam (**3**)

5.66 g (0.05 mol) of caprolactam and 6.75 ml (0.05 mol) of trimethylsilylchloride (TMSC) were dissolved in 60 ml of distilled THF. Argon atmosphere was maintained throughout the reaction. After the temperature of the reaction mixture was reached to its reflux temperature, 7.25 ml (0.05 mol) of triethylamine (TEA) was added at once. The solution was refluxed for 30 minutes, filtered, and finally THF was distilled off with a light stream of argon. The remaining yellow colored liquid was a mixture of **3** and caprolactam, so it was further purified by vacuum distillation (62 °C, 0.1 Torr). The purified material was a colorless liquid, and formed a white crystal. The chemical structure was analyzed by IR and NMR, and the thermal property was measured with DSC. m.p. 25-26 °C; ^{1}H-NMR ($CDCl_3$) 0.2 (s, 9H), 1.6~1.8 (m, 6H), 2.5 (t, 2H), 3.2 (t, 2H); ^{13}C-NMR ($CDCl_3$) 0.19, 23.61, 29.96, 31.51, 37.97, 44.62, and 183.45.

Preparation of Carboxylated PPO (**4**)

12 g of **2** was charged to the reaction flask assembled with a reflux condenser, a mercury sealed mechanical stirrer, rubber septum, and a thermocouple. 250 ml of THF was directly distilled into the flask and PPO was dissolved at 40 °C. After 4 ml of 2.5 N n-butyllithium (7.5×10^{-3} mol) was added dropwise to the polymer solution over 10 min, the reaction was allowed to proceed at 40 °C for 4 hours. The solution was then poured into a slurry of ether and dry ice, acidified with dilute HCl, and precipitated with hexane. The polymer was washed with dioxane and hexane and dried in vacuum oven at 110 °C. 4.9 mol % (per repeating unit of PPO) was the degree of carboxylation (DOC) determined by titration with 0.05 N ethanolic KOH in pyridine. 1 % thymol blue solution in ethanol was used as an indicator. ^{1}H NMR and ^{13}C NMR measurements also confirmed 4.7 mol % substitution.

Preparation of Carbonylcaprolactam substituted PPO (**6**)

12 g of **4** (0.0048 mol [-COOH]) was dissolved in 150 ml of dry carbon tetrachloride. 10 ml of thionyl chloride and catalytic amount of dimethylacetamide were added under

stirring. The reaction mixture was refluxed for 4 hours and cooled to room temperature. The remaining solvent and liquid reactant were distilled off under reduced pressure. After further treatment with high vacuum (~ 0.01 Torr) for two hours, the reaction flask was filled with freshly distilled THF (150 ml) to re-dissolve the acid chloride substituted PPO (**5**). 1 ml of **3** (0.0054 mol) was added at 0 °C, and the reaction was allowed to proceed for 30 min at 0 °C, 30 min at 25 °C , and finally for 1 h at 60 °C. **6** was then precipitated with excess methanol. It was filtered, washed with 0.05 N NaOH, 0.05 N HCl, dioxane, and methanol successively, and dried at 80 °C in vacuo. The ^{13}C NMR spectrum showed a small peak at δ176.52 due to carbonyl carbons and a shoulder at δ176.76 due to carboxylic carbon. The conversion of the carboxylic group to the carbonylcaprolactam group was calculated from the area ratio of these two peaks. Degree of substitution (DOS): 4.0 mol % per repeating unit of PPO (82 % yield).

Preparation of Graft Copolymer of PPO and Nylon 6 (**7** : Exp 1)

5 g of **6** and 10 g of purified caprolactam were charged to a round bottom flask. They were dissolved in 25 ml of dry toluene, and 0.8 ml of 2.5 N butyllithium was added at once. The reaction mixture was stirred for 36 hours at 100 °C. After cooling, 50 ml of formic acid was added under stirring, and the slurry type reaction mixture was precipitated with methanol. It was washed with methanol several times and dried at 110 °C in vacuo. PPO and Nylon 6 homopolymers were extracted with chloroform and formic acid respectably in a Soxhlet apparatus. Caprolactam conversion = 60 %; homo-PPO = 0.25 g; homo-Nylon 6 = 0.3 g.

Control experiment - Anionic polymerization of ε-caprolactam in bulk. (Control 1)

5 g of **6** and 20 g of purified caprolactam were charged into a round bottom flask. After **5** was thoroughly dissolved at 150 °C, 5 g of caprolactam containing 0.002 mol of lithiolactam was added at once. The reaction proceeded for 10 minutes at 150 °C, and then cooled down to room temperature. The rest of the experimental procedure was the same as Exp 1. Caprolactam conversion = 85 %; homo-PPO = 0.22 g; homo-Nylon 6 = 15.5 g.

Control Experiment - PPO without end-capping (Control 2)

PPO used in this experiment was not end-capped. Other synthetic conditions were the same as those of Exp 1. DOC = 4.1 mol %; DOS = 3.5 mol %. Caprolactam conversion = 35 %; homo-PPO = 0.17 g; homo-Nylon 6 = 0.55 g

Measurements

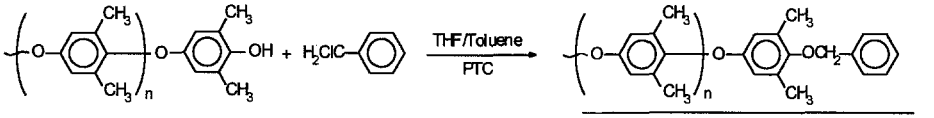
The ^{1}H NMR spectra were recorded with a Bruker AMX FT 500M Hz NMR spectrometer in 5-mm-o.d. sample tubes. A 2:4:4 (by volume) mixture of $CDCl_3$, $CHCl_2CHCl_2$, and CCl_3CH_2OH served as the solvent (1) with TMS as an internal standard. DSC measurements were carried out with a Du Pont DSC 910. The scanning speed was 10 °C/min in all cases. The FT-IR measurements of KBr pellets of polymers were performed on a Mechalson MB 102 with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

Preparation of ω-benzyl ether of PPO

The terminal hydroxyl group of PPO was end-capped because this group may lower the yield during the metalation of PPO and subsequent carboxylation. It might also lead

undesired side reactions during the anionic graft copolymerization of ε-caprolactam. **2** was prepared by the method developed by Percec and co-workers (9). TBAH acted as a phase transfer catalyst.

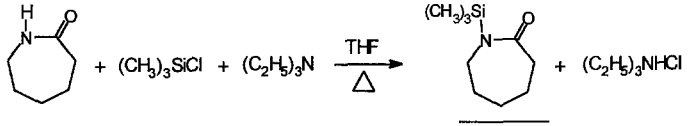


2

Conversion of the hydroxyl-terminated polymer to **2** was quantitative. Disappearance of the FT-IR peak at 3500 cm^{-1} (-OH) indicates that the expected etherification reaction occurred. It was also confirmed by ^1H NMR (disappearance of the peak at δ3.7) (9). Quantitative etherification was measured by UV spectroscopy using the method developed by McGrath (10). In this method, the unreacted terminal hydroxyl group is deprotonated with the addition of strong base - benzyltrimethylammonium hydroxide, so there appears strong absorption at 320 nm because of the phenolate anions. It was demonstrated that more than 95 % of the phenol chain end was etherized.

Preparation of N-(trimethylsilyl)caprolactam

3 was prepared by a similar method reported in the literature for the synthesis of N-trimethylsilyl-β-lactams (11). Disappearance of FT-IR peaks at 3076 and 3209 cm^{-1} (-NH) and appearance of a peak at 1251 cm^{-1} ($(CH_3)_3Si$-) indicates the occurrence of the reaction.



3

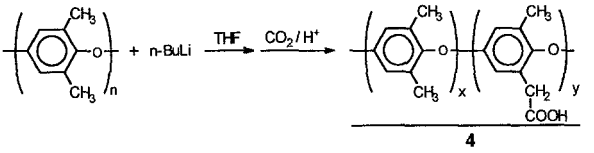
DSC thermogram of **3** shows a distinct melting point at 25 °C and a broad decomposition around 100 °C. ^1H-NMR analysis, however, revealed the existence of a small quantity of caprolactam (ca. 10 mol %).

Preparation of Carbonylcaprolactam substituted PPO

Carboxylated PPO (**4**) was prepared by metalation of PPO with n-butyllithium followed by treatment with an excess of carbon dioxide. The details of the method can be found elsewhere (7,12~14). The carboxyl group of **4** was modified by thionyl chloride to introduce acid chloride group. Acid chloride group of **5** was reacted with **3** under elimination of trimethylsilylchloride to give **6**. There may also be two other methods for the preparation of **6** as suggested by Kricheldorf (11). The first method is to react **5** with metallic salt of caprolactam. The second is to react **5** with caprolactam in a high boiling solvent using tertiary amine as an acid acceptor. These two methods, however, resulted in crosslinked products because of the high reactivity of the acid chloride. The gel type product was not dissolved in any solvent even at elevated temperature and prolonged period.

Figure 1 shows the IR spectrum of the modified PPOs. As the modifications have progressed, the position of carbonyl peak moves from 1720 cm^{-1} (**4**) to 1800 cm^{-1} (**5**), and 1700 cm^{-1} (**6**). Tgs of these materials are 200 °C (**1**), 198 °C (**2**), 210 °C (**4**), and 213 °C (**6**)

respectably when measured by DSC. GPC results show that there is little change in molecular weights during these modifications.



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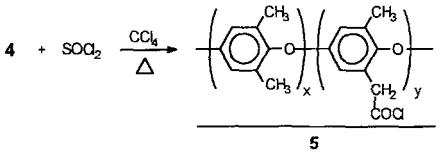

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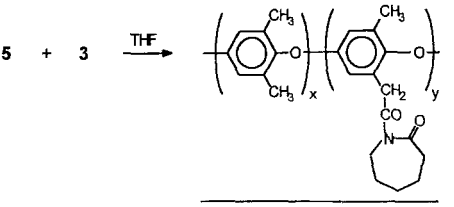
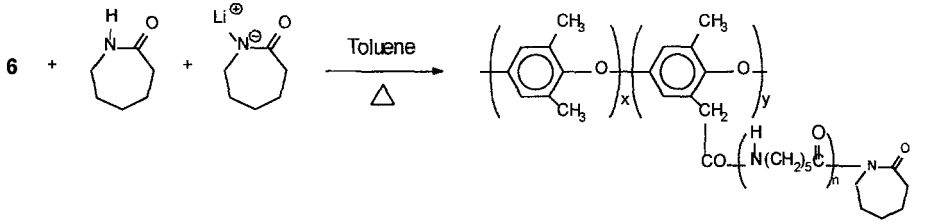


6

Preparation of PPO-g-Nylon 6(7)

7 was prepared by the anionic graft copolymerization of ε-caprolactam on the macroinitiator 6 in toluene solution using lithiolactam as a catalyst.



7

It has been reported by Wondraczek and Kennedy (15) that copolymerization carried in solution gave higher block efficiencies than those in bulk because of the increased miscibility between the polymer and caprolactam. Previously most of the caprolactam polymerizations have been conducted in bulk states. For PPO and caprolactam system, however, there are some problems. First, this mixture forms a homogeneous solution above 120 °C. The reaction temperature should be higher than 120 °C, but even at 130 °C, the reaction proceeds too fast to be controlled. Second, side reactions, for example chain scission and branching (16), start to compete with the chain propagation. These often lead to a cross-linked product. Third, caprolactam should serve as the solvent for PPO, so there is a limitation for the ratio of PPO to caprolactam. It means that the composition of the

Table 1. Characterization of the graft copolymer of PPO and Nylon 6

sample code	DOS (*1) (mol %)	number of graft sites per PPO chain	$\overline{M}_n$ of grafted Nylon	solution property(*2)
Exp 1	4.0	3.2	3700	clear solution
Exp 2(*3)	4.3	1.1	2500	clear solution
Control 1	4.0	3.4	3200	highly gelled
Control 2	3.5	3.7	660	highly gelled

*1 Degree of substitution of carbonylcaprolactam group on PPO

*2 After dissolving the copolymer sample in solvent, the existance of crosslinked product was determined qualitatively.

*3 It was prepared with the same experimental procedure as Exp 1 besides the $\overline{M}_n$ of PPO was 3000.

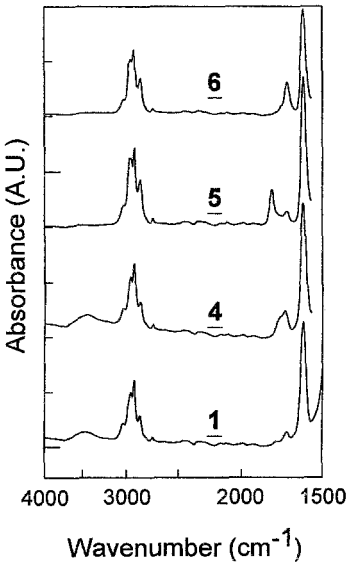


Figure 1. IR spectra of modified PPOs.

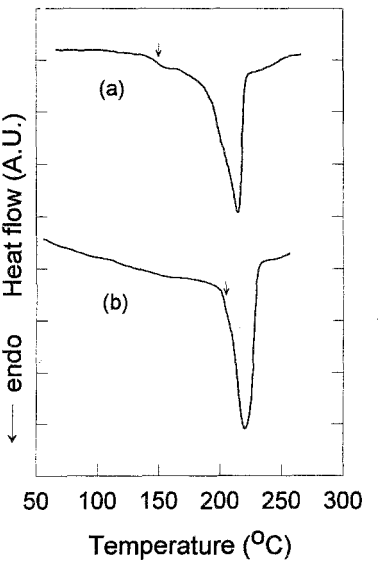


Figure 2. DSC thermograms of PPO-Nylon 6 graft copolymers. Arrow represents the Tg of homo-PPO.
(a) $\overline{M}_n$ (PPO) = 3000
(b) $\overline{M}_n$ (PPO) = 9800

copolymer can not be varied freely. All these problems may be settled if the reaction is conducted in solution. Table 1 shows the results of the graft copolymerization under various conditions. The graft ratios of Nylon 6 to PPO were calculated from the area ratio of δ39.35 (Nylon, α carbon) and δ114.27 (PPO, unsubstituted ring) in ^{13}C NMR. The number of graft sites per PPO chain was calculated from the area ratio of δ33.61 (PPO, methylene) and δ114.27 in ^{13}C NMR. With these two values, we could calculate the $\overline{M}_n$ of grafted Nylon 6 chain. In all cases, the numbers of graft sites are very close to those of functional groups. It means the carbonylcaprolactam group is very efficient for the initiation of the anionic graft copolymerization of caprolactam. When the reaction was carried out in the bulk state, however, a large amount of homo-Nylon was formed and the graft copolymer obtained was highly crosslinked. It also shows that terminal hydroxyl group took a roll of chain transfer during the reaction. To the contrary, both the graft ratio and grafting efficient were high when the reaction proceeded in toluene solution. DSC thermogram of the graft copolymer (Figure 2(a)) shows a melting point(T_m) of Nylon 6 segment at 220 °C. However, the glass transition temperature of PPO is not shown here because it is very close to T_m of Nylon 6. When the molecular weight of PPO is 3000, the T_g is low enough to be isolated from the T_m of Nylon 6 (Figure 2(b)). This copolymer (Exp 2 in Table 1) was prepared by the same method as Exp 1 except that the $\overline{M}_n$ of the base material, PPO, is 3000 and $\overline{M}_w / \overline{M}_n$ is 1.25. The number of graft sites per PPO chain was 1.1, and the $\overline{M}_n$ of the grafted Nylon is 2500. Though transparent was the casted film from a solution, this copolymer showed phase separated behavior when measured by DSC.

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