BLOCK COPOLYMERS POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE)–POLY(6-HEXANELACTAM). PREPARATION AND COMPOSITION

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Received February 25, 1993
Accepted April 26, 1993

Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Poly(2,6-dimethyl-1,4-phenylene oxide)–poly(6-hexanelactam) diblock copolymers were prepared from low-molecular weight poly(2,6-dimethyl-1,4-phenylene oxide) by transforming its phenolic end groups via the reaction with 2,4-tolylene diisocyanate and 6-hexanelactam to polymeric initiators and the subsequent anionic polymerization of 6-hexanelactam. The polymerization of 6-hexanelactam was carried out in bulk or toluene solution. The content of the 6-hexanelactam homopolymer was estimated by TLC showing that the pure diblock copolymer can be prepared in toluene. The reason for relatively low yields is discussed.

The endeavour at preparing poly(phenylene oxide) blends, particularly those of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polyamides is manifested by a high number of patents published in the last years. Such blends are expected to combine favourable properties of PPO, such as high thermal and dimensional stability, with the good properties of polyamides, like solvent and chemical resistance and good processability. Both types of polymers are incompatible and their blending requires the addition of a third component acting as an interfacial agent often called compatibilizer.

Few block and graft copolymers containing chemically linked PPO and polyamide chains which are suitable as compatibilizers were described[1 – 3]. Some patents and papers[4 – 7] deal with PPO bearing groups which are able to react with amine end groups of polyamide chains and to form such copolymers during polymer blending.

It has been the aim of the present work to synthesize diblock copolymers by transforming the phenolic end groups of PPO to the *N*-acyllactam groups acting as the centres initiating the growth of polyamide chain in the anionic polymerization of 6-hexanelactam (HL). Block copolymers of this type are supposed to act as efficient polymeric surfactants.

EXPERIMENTAL

Materials

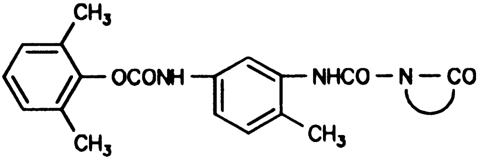
Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) oligomer was obtained as a waste product from the pilot-plant PPO production in the Research Institute of Macromolecular Chemistry, Brno, or prepared as described below. 2,6-Dimethylphenol of polymerization grade (Spolana, Neratovice) was distilled in vacuum before polymerization. The oxidation polymerizations were carried out in toluene at 20 °C with the CuCl–4-dimethylaminopyridine catalyst[8]. 2,4-Tolylene diisocyanate (TDI; Fluka, purity > 98%) was redistilled.

6-Hexanelactam (HL), toluene and *N*,*N*-dimethylacetamide (DMA) were purified and dried as described earlier[9]. Potassium 6-hexanelactamate (KL) was prepared from potassium *tert*-butoxide and HL[10].

N-{[5-(2,6-Dimethylphenoxycarbonylamino)-2-methylphenyl]carbamoyl}-6-hexanelactam (*I*) was prepared as a model by reacting equimolar amounts of TDI and 2,6-dimethylphenol in boiling toluene for 3 h, adding equimolar amount of HL and refluxing for 12 h. Chromatographic separation of the reaction mixture on a silica gel column by elution with cyclohexane–diethyl ether mixtures and crystallization from cyclohexane–chloroform gave the product melting 162 – 163 °C in 32.6% yield. For $C_{23}H_{27}N_3O_4$ (409.5) calculated: 67.46% C, 6.65% H, 10.26% N; found: 67.48% C, 6.63% H, 10.21% N. IR spectrum (KBr disk): 3 300, 3 125, 2 925, 1 740 (C=O), 1 693 (C=O), 1 650, 1 605, 1 545 cm^{-1}.

Preparation of PPO Initiator

A solution of 5 g PPO (approx. 0.5 – 0.8 mmol) in 50 ml dry toluene was added dropwise under inert atmosphere to the boiling solution of 0.4 ml (2.6 mmol) TDI in 100 ml toluene during 2 h and the mixture was refluxed for another 6 h. Then, 0.6 g (5.3 mmol) HL was added, the mixture was refluxed for 8 h, cooled and precipitated in 700 ml ethanol. The product was separated by filtration and dried at 60 °C/260 Pa. Alternatively, the reaction with TDI was carried out at ambient temperature for 140 h in the presence of 8 μl dibutyltin dilaurate. The reaction was monitored by the decrease in IR absorption of isocyanate groups at 2 270 cm^{-1} in the withdrawn samples precipitated in acetone.



I

Characterization of PPO Initiators

Intrinsic viscosity [η] of toluene solutions (c = 0.4 – 1.2 g dl^{-1}) was determined at 25 °C in an Ubbelohde viscometer with capillary diameter 0.42 mm and used for the $\overline{M}_n$ calculation from the relation $[\eta] = 3.8 \cdot 10^{-4} \overline{M}_n^{0.73}$ (ref.[11]). $\overline{M}_n$ and $\overline{M}_w$ were obtained by SEC run with a H-P 1090 liquid chromatograph and a H-P 1037A differential refractometer on a 600 × 7.5 mm column with PLgel 10 μm MIXED (Polymer Laboratories) using THF as a mobile phase and calibration with polystyrene standards (molecular weight range 60 – 3 200 000). The $\overline{M}_n$ values were also determined by vapor-pressure osmometry of chloroform solutions measured with a Hitachi Perkin–Elmer model 115. Terminal *N*-carbamoyllactam groups were determined by IR spectrometry (Perkin–Elmer 457 spectrometer) of CCl_4 solutions in 0.1 mm and 0.2 mm KBr cells against the solution of non-functionalized PPO of the same concentration (50 mg ml^{-1}) at 1 713 cm^{-1}. The calibration was carried out with the model compound *I* (ε = 0.173 l cm mol^{-1}) in the CCl_4 solution of non-functionalized PPO.

Block Copolymerization

a) *In bulk*: The PPO initiator and a part of HL were dried together in a polymerization ampoule and the remaining HL in a flask for the preparation of the KL solution, both at ambient temperature and 60 Pa. The ampoule contents were homogenized at 90 – 150 °C in an inert atmosphere, cooled to 90 – 120 °C, mixed with the solution of KL in HL and polymerized in a 150 °C bath. The cooled product was crushed or cut, extracted twice with boiling aqueous ethanol and dried at 60 °C/260 Pa to determine the conversion of HL. The product was freed from non-copolymerized PPO by extraction with warm toluene on sintered glass filter and dried again in vacuum at 60 °C. The fraction of non-reacted PPO initiator was calculated by difference.

b) *In solution*: 4.000 g HL was predried in a 50 ml polymerization vessel equipped with a magnetic stirrer, reflux condenser, and inlet and outlet of inert gas. The separately prepared KL was dissolved in HL at 80 – 90 °C and cooled; then 1.000 g of PPO initiator in 7.00 ml dry toluene or toluene–DMA was added and the mixture was polymerized while stirring and refluxing in a 120 °C bath. The reaction mixture was diluted with 50 ml toluene, the block copolymer was separated on a sintered glass filter, washed with toluene and methanol and dried at 60 °C/260 Pa. The toluene filtrate was concentrated in vacuum, the nonincorporated PPO was precipitated into 150 ml ethanol, separated by filtration and dried.

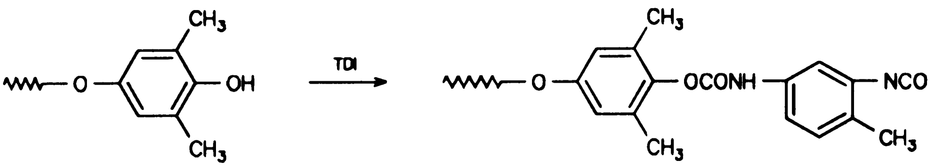
Thin Layer Chromatography of Polymers

Approximately 20 μg of the block copolymer or of poly(6-hexanelactam)–PPO mixture as a standard in a solution containing 1 – 2 mg of the polymers in 0.1 ml of a 1 : 1 (v/v) mixture of formic acid and chloroform was applied onto a 0.2 mm layer of Kieselgel GF_{254} (Merck) on a 5 × 25 cm glass plate, dried, developed with formic acid–water (25 : 10 v/v) and thoroughly dried. The block copolymers remain on the start and quench the 254 nm UV light whereas homopolyamide forms a 1.5 – 2.2 cm long spot with the centre at R_F 0.63 – 0.68 detected by iodine vapor. A weak tail from the start up to R_F 0.10 – 0.15 quenches the UV light and is due to the diblock copolymers with short PPO blocks. The absence of PPO in the extracted product can be proved by developing the plate in toluene where PPO travels in the front.

RESULTS AND DISCUSSION

Preparation of PPO Initiators

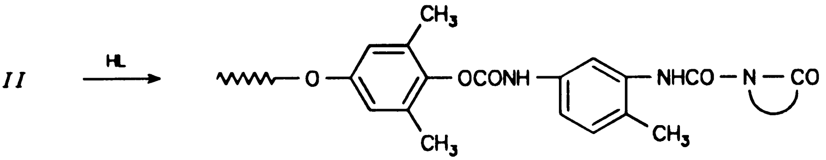
The PPO initiators of the anionic lactam polymerization used in this work are low-molecular-weight PPO ($\overline{M}_n$ = 6 000 – 15 000) with one terminal phenolic group in each molecule functionalized by the reactions with an excess of TDI and HL.



PPO

II

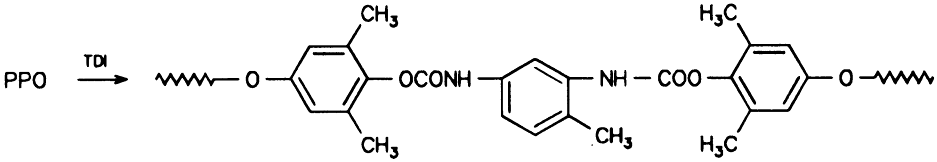
(A)



III

(B)

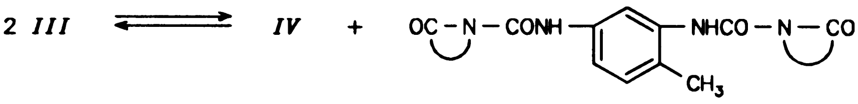
An oligomeric product from the production of PPO was used first. The presence of terminal OH groups was proved by ^{13}C NMR spectra (δ 144.5 ppm in $CDCl_3$). As the results of functionalization and block copolymerization were not satisfactory, low-molecular-weight PPO were prepared by the method[8] giving the defined polymer with one OH group per chain. The starting PPO and the functionalized products are characterized in Table I. The number average molecular weights $\overline{M}_n$ were obtained from intrinsic viscosity $[\eta]$ of their toluene solutions. The $\overline{M}_n$ data from SEC are in good agreement with the viscometric data though the former are derived from the direct calibration with polystyrene standards. A considerable increase in $\overline{M}_n$ in the functionalization can be ascribed to the coupling reaction:



(C)

IV

The coupling occurred in spite of the different reactivity of the two NCO groups in TDI and using functionalization conditions which usually suppress it to a minimum, viz. a slow addition of PPO to an excess of TDI. The concentration of *N*-carbamoyllactam end groups in the PPO initiators *III* (Table I) was estimated by IR spectrometry. The yield of functionalization, estimated from the concentration of the end groups ([I]) and the viscometric $\overline{M}_n$, ranges between 25 and 61% (Table I). The same yields were obtained in the functionalization step carried out in toluene in the absence of catalyst at 100 °C or under catalysis of dibutyltin dilaurate (0.6 mole % related to TDI) at 20 °C. Obviously, most of the coupling takes place as a side reaction through the exchange of the lactam grouping which is slower and requires higher temperature.

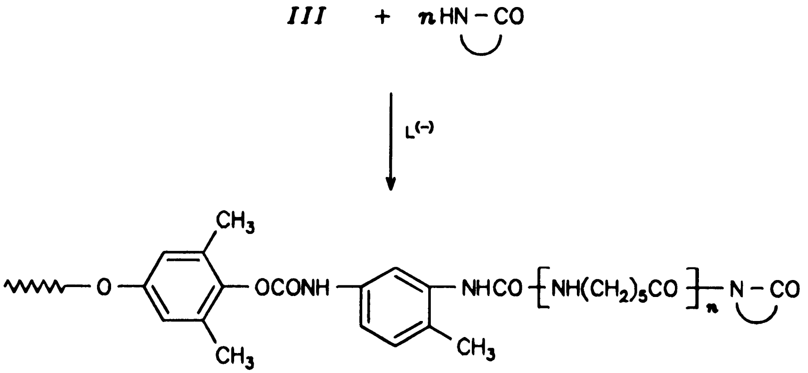


V

(D)

Preparation and Composition of Block Copolymers

A polyamide block was built on the terminal *N*-carbamoyllactam group of PPO initiator *III* by acylation of the HL anion ($L^{(-)}$; activated monomer) as is usual in the anionic polymerization of lactams[12].



VI

(E)

The copolymerization without solvent is limited by the solubility of PPO in the melt of HL. Up to about 40 wt.%, PPO oligomers form a solution in HL at 120 °C which can be mixed with the solution of potassium 6-hexanelactamate (KL) in HL and polymerized. The copolymers *VI*, runs 1 and 2 in Table II, were prepared in this way. The polymerization mixtures rapidly solidified due to the incompatibility of polyamide and PPO blocks without reaching a high conversion of HL and PPO. The product was nonhomogeneous and was therefore characterized as a whole.

In order to keep the PPO initiator and activated monomer in contact for a longer time, further polymerizations were carried out in solution, most of all in toluene, similarly as in the case of polystyrene–polyamide block copolymers[9]. The conversions of

HL were even lower than in the bulk copolymerization due to the precipitation of block copolymer but the product was more homogeneous. The PPO homopolymer remained dissolved in toluene and was separated and recovered by precipitation in ethanol. The conversion of PPO to the copolymer corresponding to the difference between the used and recovered PPO (Table II) was always higher than that calculated from the elemental analysis of the copolymer. This discrepancy may be caused by solubility of the block copolymer with short PPO and polyamide blocks in ethanol.

The SEC data in Table I show that the recovered PPO has higher $\overline{M}_n$ than the starting PPO, i.e. closer to the corresponding functionalized PPO. Also, the lower $\overline{M}_w$ values and hence a narrower distribution of molecular weights indicate that the coupled molecules of PPO are recovered and the shorter molecules are consumed as initiators.

The conversion of HL can be increased by using the mixed solvent toluene – *N,N*-dimethylacetamide (DMA) which retains the growing polyamide block in solution for a longer time (Table II, runs 11 and 12).

Because the copolymerization proceeds under conditions of the base-catalyzed PPO functionalization, the exchange reaction (*D*) may occur and form the low-molecular-weight initiator *N,N'*-(2,4-tolylenebiscarbamoyl)bis-6-hexanelactam (*V*). The thermal

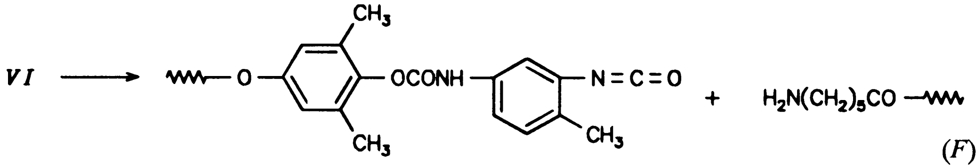
TABLE I

Characteristics of starting poly(2,6-dimethyl-1,4-phenylene oxides) (PPO) (A, B, C, D), corresponding PPO initiators *III* (A1, A2, B1, C1, D1, D2) and PPO recovered from 6-hexanelactam polymerization (B0, C0)

PPO	$\overline{M}_n$ (visc)	$\overline{M}_n$ (VPO)	$\overline{M}_n$ (SEC)	$\overline{M}_w$ (SEC)	$[I] \cdot 10^6$ [a] mol g^{-1}	Yield[b] %
A[c]	6 470	–	3 590	8 520	0	–
A1	8 190	5 940	6 920	12 300	82.6	53
A2	8 600	–	7 690	13 600	87.7	57
B	14 800	–	–	–	0	–
B1	15 100	14 500	14 600	34 200	35.3	52
B0[d]	15 440	–	16 240	19 600	–	–
C	6 950	8 150	8 990	17 000	0	–
C1	10 200	–	11 400	23 000	45.9	25
C0[e]	11 820	–	11 300	19 800	–	–
D	10 400	8 850	11 800	24 750	0	–
D1	16 300	17 700	12 000	24 800	58.7	61
D2[f]	16 800	–	14 800	32 600	44.8	46

[a] Concentration of *N*-carbamoyllactam end groups; [b] of functionalization; [c] oligomers from the PPO production; [d] recovered from run 4, [e] recovered from run 5 (see Table II); [f] the first functionalization step performed at ambient temperature (see Experimental).

dissociation of existing urethane or urea groupings in PPO coupling products *IV* (the reverse reaction (*C*)), in PPO initiator *III* and its precursor *II* (reverse reactions (*B*) and (*A*)) and in block copolymers *VI* reaction (*F*), which give isocyanate groups, can also be assumed.



(*F*)

VI

TABLE II

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO)–poly(6-hexanelactam) (PA) block copolymers *VI* prepared by the anionic polymerization of 6-hexanelactam (HL) initiated with PPO initiators *III* and catalyzed with potassium 6-hexanelactamate (KL)

Run	*III*	[KL] mole %	Conversion wt. % HL	Conversion wt. % PPO	PPO block, wt. fraction ex conversion	PPO block, wt. fraction ex N content	PA block $\overline{M}_n$[a]	PA homopolymer[b]
1[c,d]	A1	0.80	34.3	42.6	0.237	0.131	–	+
2[c,e]	A2	0.53	24.8	13.6	0.566	0.519	–	+
3[f]	A2	0.60	4.5	2.7	0.131	0.098	59 600	–
4[f]	B1	0.40	3.1	8.9	0.419	0.237	47 600	–
5[f]	C1	0.50	5.4	9.3	0.299	0.096	65 400	–
6[f]	D1	0.66	10.4	7.9	0.158	0.102	91 600	–
7[f]	D1[g]	0.40	3.6	7.6	0.344	0.141	–	–
8[f]	D1[h]	0.40	6.5	9.2	0.261	0.160	–	–
9[f]	D1[i]	0.40	1.3	1.6	0.233	–	–	–
10[f]	D2	0.40	2.7	3.5	0.246	0.242	32 600	–
11[j]	D1	0.40	18.2	14.9	0.169	0.090	–	+
12[k]	D1	0.40	8.2	32.4	0.500	0.420	–	+

[a] Calculated from $\overline{M}_n$(visc) of starting PPO (Table I) and N content; [b] TLC detection: – negative, + detected, ++ high content; [c] in bulk, 150 °C/30 min; [d] PPO/HL = 1 : 5, [e] PPO/HL = 1 : 1.5; [f] in toluene under reflux, 6 h; [g] recovered and refunctionalized *III* from run 6, [h] the same from run 7, [i] the same from run 8; [j] in toluene–DMA 2 : 1 (v/v) under reflux, 6 h; [k] in toluene–DMA 1 : 1 (v/v) under reflux, 6 h.

In this way, the chains of PPO initiator can be generated but also both homopolymers can be formed. A TLC method was developed, in which separation is based on the chemical composition and not on the molecular weight using a selective detection by UV light quenching. The method detects the presence of about 1 wt.% of HL homopolymer in the block copolymer *VI*.

Surprisingly, the products prepared by copolymerization in toluene do not contain detectable amounts of HL homopolymer. This may be caused by the early precipitation of the block copolymer from the solution preventing it from a cleavage to homopolymers. The initiator of homopolymerization *V* is not formed. On the other hand, the homopolyamide was found in the products of copolymerization carried out in mixed solvents toluene–DMA, showing that the homopolyamide is formed rather by the cleavage of the urethane group between polymer blocks in the homogeneous phase. The products of the copolymerization without solvent contain considerable amounts of homopolyamide, probably because of the higher temperature used.

Repeated Functionalization of PPO

Assuming that the low incorporation of PPO into block copolymers is caused by coupling (reactions (*C*) and (*D*)) and other side reactions and not only by the absence of OH end groups in the starting PPO, the recovered PPO should be able to undergo a new functionalization and could be reused as the initiator. This proved true in three repeated sequences recovery – refunctionalization – reuse, indicated in Table II as successive runs 7, 8, 9. Only the fourth run 9 gave a very low yield of the block copolymer.

The recovered PPO obviously contained a fraction of block copolymer with very short polyamide blocks because it dissolved in cold toluene to a turbid solution in some cases. The turbidity increases with the number of reuses so that the PPO recovered from the copolymerization run 9 (Table II) cannot be completely dissolved even in boiling toluene.

CONCLUSIONS

The terminal phenolic groups of PPO can be transformed to the initiator groups of the anionic lactam polymerization by reactions with a diisocyanate and a lactam. This functionalization is, however, complicated by extensive chain coupling. Pure poly(2,6-dimethyl-1,4-phenylene oxide)–poly(6-hexanelactam) diblock copolymers were prepared in low yields from these PPO initiators by the anionic copolymerization in toluene. The diblock copolymers were used for the study of thermal properties and compatibilization of homopolymer blends in solution which is reported in a further paper.

This work was supported by the research grant No. 45018 of the Grant Agency of Academy of Sciences of the Czech Republic. The authors thank to Mrs K. Brzkovská for technical assistance.

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Translated by the author (J. S.).