

NOTES

Grafting of Hydrophobic Oligostyrene onto Hydrophilic 6,6-Type Polyamide

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(Received May 8, 1992)

KEY WORDS Grafting / Hydrophilic Polyamide / Semitelechelic Oligostyrene / Amphiphilic Copolymer / Glass Transition Temperature /

Graft copolymers composed of hydrophilic and hydrophobic polymer segments have been known to be promising as amphiphilic, biocompatible polymeric materials. Recently, tailored graft copolymers have been synthesized by the macromonomer technique. For instance, Nakashima *et al.* prepared graft copolymers consisting of hydrophilic poly(2-hydroxyethyl methacrylate) as a backbone and hydrophobic poly(methyl methacrylate) (PMMA) as a branch.¹ Tsukahara *et al.* synthesized graft copolymers composed of hydrophilic poly(2,3-dihydroxypropyl methacrylate) as a backbone and hydrophobic polystyrene as a branch.² In addition, Chujo *et al.* prepared graft copolymers by a combination of aromatic polyamide as a backbone with PMMA as a branch for the purpose of a surface modifier of commodity polymers.³ The macromonomer technique is the most useful method to prepare graft copolymer having branches with welldefined length,⁴ but the construction of backbone by copolymerization of macromonomers with comonomers seems to be obscure in regard to the sequence and length.

Previously, we reported the interfacial polycondensation of (2*R**,4*S**)-4-chloroformyl-2-chloroformylmethyl-2,4-dimethyl-4-

butanolide with 1,6-hexanediamine.⁵ This reaction was accompanied by a partial hydrolytic cleavage of the γ -lactone ring (ring-opening ratio of about 0.35—0.55), and gave an unique 6,6-type polyamide (PA-6L) containing at random both γ -lactone ring and hydrophilic groups such as carboxyl and hydroxyl groups. This polyamide promises well as a tailor-made backbone for grafting, because it has functional side chain groups.

This paper describes the preparation of graft copolymers consisting of hydrophilic PA-6L as a backbone and hydrophobic oligostyrene (OST) as a branch by coupling between the hydroxyl-containing PA-6L and chloroformyl-semitelechelic OST (Scheme 1). Furthermore, characterization of the resulting graft copolymer is presented. The structure of the graft copolymers synthesized in this study is shown in Scheme 2.

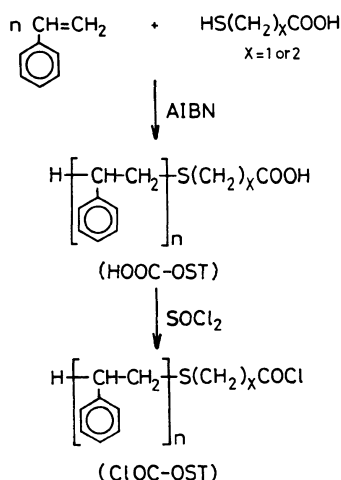
EXPERIMENTAL

Materials

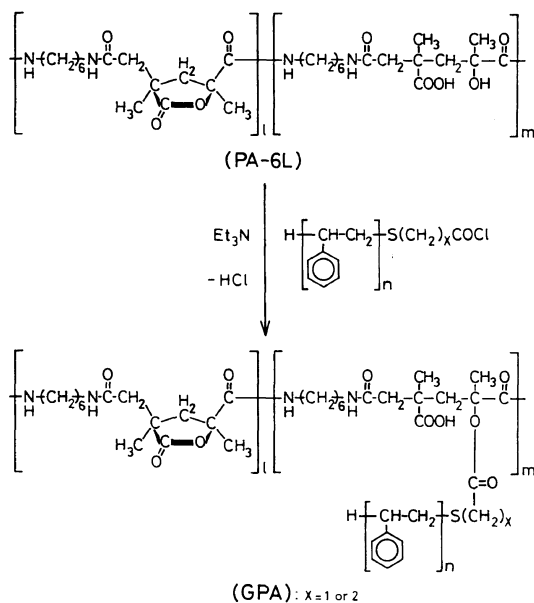
The original PA-6L for grafting was prepared according to the method described in the previous paper.⁵ Commercial styrene was purified by an usual method. Commercial tetrahydrofuran (THF), *N,N*-dimethylform-

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Scheme 1. Synthesis of the semitelechelic oligostyrenes.



Scheme 2. Synthesis of the graft copolymers.

amide (DMF), and *N,N*-dimethylacetamide (DMA) were dried over calcium hydride and distilled before use. Other reagents and solvents were commercially obtained and used without further purification.

Characterization of Samples

IR spectra were measured with a JASCO

REPORT-100 spectrophotometer. The number-average molecular weight (\bar{M}_n) of carboxyl-semitelechelic OST was determined by gel permeation chromatography (GPC) data obtained in THF using a Hitachi 635 chromatograph equipped with Shodex A-803, KF-802, and KF-801 columns in series. These data were calibrated with polystyrene standards. The carboxyl-group content was determined by titrating the OST in THF with 0.02 *N* KOH_{aq}, using phenolphthalein as an indicator.⁶ The intrinsic viscosity $[\eta]$ of PA-6L was measured with a Ubbelohde viscometer at 25°C. The viscosity-average molecular weight (\bar{M}_v) of PA-6L was calculated by Elias's equation for polyamide-66.⁷ Thermodiagrams of polymers were recorded with a Rigaku-Denki Thermoflex DSC-8230. A DSC sample of about 4 mg was heated at 20°C min⁻¹ from -50 to 180°C under a nitrogen atmosphere. The ring-opening ratio, $m/(l+m)$, of PA-6L was determined from absorbance (*A*) on IR spectrum (film): $A_{1700}/(A_{1780} + A_{1700})$.

Preparation of Carboxyl-Semitelechelic OST

In a 50 ml three-necked flask, styrene (10.0 g, 0.10 mol), a prescribed amount of mercaptoacetic (MCAA) or mercaptopropionic acid (MCPA) as a chain transfer agent, and AIBN (0.136 g, 8.29×10^{-4} mol) were placed. Oligomerization was carried out at 60°C for 5 h under a nitrogen atmosphere. The resulting OST was precipitated by adding into methanol, purified twice by reprecipitation of the benzene solution by pouring into methanol, then dried *in vacuo*: colorless and translucent powder; IR (KBr-disk) 2930, 2850 (-CH₂-), 1710 (C=O), 1600, 1490, 1450, 760, and 700 cm⁻¹ (-Ph). *Anal.* Found: C, 90.37%; H, 8.46%. Calcd for C₅₀₈H₅₁₀O₂S: C, 91.34%; H, 7.70%.

Preparation of Chloroformyl-Semitelechelic OST

A mixture of the above carboxyl-semitelechelic OST (0.34 g, 4.94×10^{-5} mol) dis-

solved in THF (20 ml) and thionyl chloride (2.01 g, 1.69×10^{-2} mol) was heated at 60°C for 12 h. After the reaction, the solvent and unchanged thionyl chloride were evaporated off *in vacuo* to afford a crude chloroformyl-semitelechelic OST, which was used without further purification: IR (KBr-disk) 2930, 2850 ($-\text{CH}_2-$), 1790 ($\text{C}=\text{O}$), 1600, 1490, 1450, 760, and 700 cm^{-1} ($-\text{Ph}$).

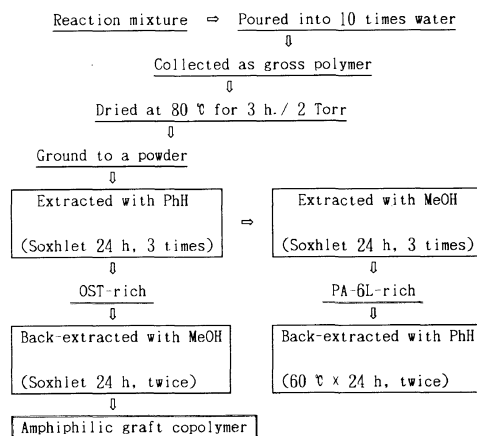
Typical Grafting of PA-6L

To a mixture of PA-6L (0.4 g, 4.94×10^{-5} mol) and triethylamine (0.01 g, 9.88×10^{-5} mol) in DMF (20 ml), a solution of the above acid chloride in THF (10 ml) was added dropwise at -3 – 0°C , and the resulting mixture was stirred at r.t. for 24 h. After the reaction, the reaction mixture was treated as shown in Scheme 3.

RESULTS AND DISCUSSION

Synthesis of Semitelechelic OST

The oligomerization of styrene with MCAA or MCPA was carried out for preparing of carboxyl-semitelechelic OST. The thiol compound was chosen as a chain transfer agent since it is known to be suitable both for controlling the molecular weight and for introducing carboxyl group at a chain end of the radically oligomerized styrene.^{8,9} Table I shows that the yield and molecular weight of carboxyl-semitelechelic OST is reduced with increasing amount of thiol. This result indicates that the molecular weight of carboxyl-semitelechelic OST may be controlled to a certain extent by the ratio $[\text{thiol}]/[\text{styrene}]$. The functionality was determined by titration of the carboxyl end group, which was effectively introduced at one end of the OST chain. The chlorination of carboxyl-semitelechelic OST was confirmed by the IR spectra: a new absorption band at 1790 cm^{-1} due to the $-\text{COCl}$ group appeared by the chlorination. The chloroformyl-semitelechelic OST was immediately used for the grafting without



Scheme 3. Separation procedure of the graft copolymers.

Table I. Preparation of carboxyl-semitelechelic oligostyrene^a

Thiol	Molar ratio ^b	Yield	$\bar{M}_n \times 10^{-3c}$	Functionality ^d
		%		
MCAA	0.10	24	6.7	0.94
	0.30	11	4.8	0.95
MCPA	0.05	23	7.7	1.01
	0.10	13	6.8	0.99
	0.30	5	5.9	—
	0.50	1	3.7	—

^a Reaction temp, 60°C ; reaction time, 5 h.

^b $[\text{Thiol}]/[\text{Styrene}]$.

^c Determined from GPC.

^d Number of COOH -groups per molecule.

further purification.

Synthesis and Characterization of PA-6L-g-OST Copolymers

As shown in Scheme 2, the graft copolymers were prepared by the reaction of hydroxyl-containing PA with chloroformyl-semitelechelic OST in the presence of triethylamine as an acid acceptor. The resulting graft copolymers were separated according to the procedure shown in Scheme 3. Table II shows the conditions and results for the synthesis of graft copolymers. Table III shows the results

Table II. Preparation of graft copolymers^a

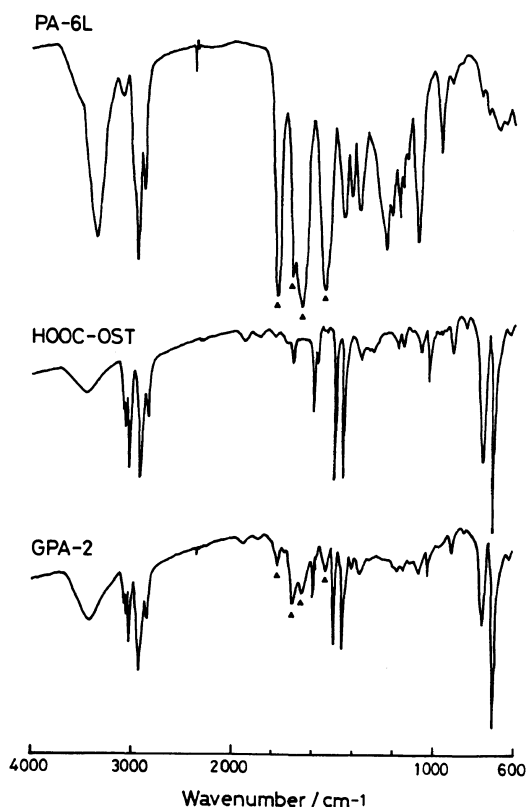
Sample code	PA-6L			OST ^d	Solvent	Yield ^e %
	$\bar{M}_v \times 10^{-3}$ ^b	$m/(l+m)$	-OH ^c			
GPA-1	9.4	0.36	11	6.7	DMF	17
GPA-2	8.1	0.51	14	6.8		
GPA-3	6.0	0.41	8	6.8		
GPA-4	4.0	0.56	7	6.7		
GPA-5	4.0	0.56	7	4.8	DMA	29

^a [PA-6L]/[OST] = 1 (molar ratio).^b Calculated from $[\eta]$ by Elias's equation.⁷^c Average number of OH group: average degree of polymerization $\times m/(l+m)$.^d $\bar{M}_n \times 10^{-3}$ (see Table I).^e (Weight of back-extract by methanol/total weight of PA-6L and OST) $\times 100$.**Table III.** Comparison of extraction behavior between graft and blend polymers

Sample code	wt/wt ^a			
	$E_{\text{PhH}}/O_{\text{ST}}$	$B_{\text{MeOH}}/E_{\text{PhH}}$	$E_{\text{MeOH}}/PA-6L$	$B_{\text{PhH}}/E_{\text{MeOH}}$
GPA-1	1.14	0.32	0.88	0.03
GPA-2	1.11	0.74	0.79	0.02
GPA-3	1.48	0.34	0.30	0.14
GPA-4	1.29	0.21	0.53	0.05
GPA-5	1.08	0.43	0.25	0.10
Blend ^b	1.00	0	1.00	0

^a E, extraction; B, back-extraction.^b [PA-6L]/[OST] = 1 (molar ratio).

of the extraction behavior of graft copolymers, comparing to that of a blend polymer of PA-6L and HOOC-OST (1:1). Homo-OST is soluble in benzene, but hardly soluble in methanol, opposite homo-PA-6L which is insoluble in benzene, but easily soluble in methanol. In the blend polymer, the OST part was actually extracted completely by benzene, while the PA-6L one by methanol. On the other hand, the graft copolymers showed an unbalanced extractability. That is, the first extract by benzene was an OST-rich component, and the next one by methanol was PA-6L-rich. There was no insoluble part in both

**Figure 1.** IR spectra of homopolymers and graft copolymer.

solvents. Each extract was further back-extracted by the counter solvent in consideration of the amphiphilic property of graft

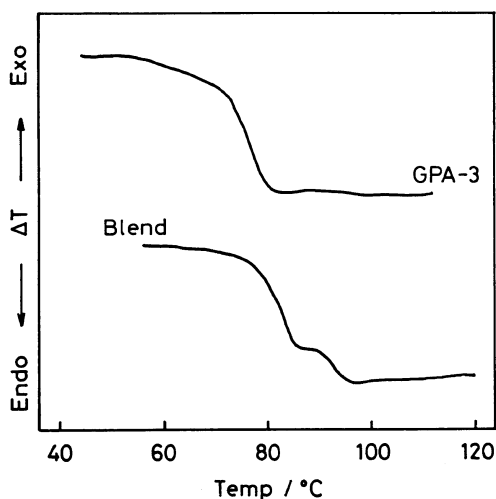


Figure 2. DSC curves of graft and blend polymers.

copolymer. An amphiphilic graft copolymer was collected from the first benzene extract by back-extraction using methanol.

The IR spectrum of graft copolymer GPA-2 is illustrated in Figure 1 comparing with those of original PA-6L and carboxyl-semitelechelic OST. The absorption peaks corresponding to both homopolymers are observed in the spectrum of GPA-2. The absorption peaks marked (\blacktriangle) in Figure 1 correspond to the carbonyl ones owing to γ -lactone ring, carboxyl group, and amide linkage. As the decrease of hydroxyl absorption peak at 3340 cm^{-1} is observed in the spectrum of GPA-2, the hydroxyl group seems to be the effective grafting site. The composition of graft copolymers is also supported by the comparison of those ^1H NMR spectra. The elemental analysis of GPA-2 indicates that one molecular unit of PA-6L backbone is grafted by two or three branches of OST

(Found: C, 81.26%. Calcd as two branches: 79.54%, as three ones: 82.45%).

Figure 2 shows the DSC curves of graft copolymer GPA-3 and a blend polymer of PA-6L and HOOC-OST (1:1). Only single glass transition temperature (T_g) is observed at 73°C for the GPA-3, while the blend polymer has two T_g at 78 and 91°C . As homopolymers, PA-6L and HOOC-OST, have T_g of 88 and 101°C , respectively, it is considered that the amphiphilic graft copolymer is composed of a homogeneous phase.

Acknowledgments. The authors wish to thank Mr. Tetsuji Kodaira of GE Plastics Japan Ltd. for the measurement of DSC curves of polymers. We are also grateful to Dr. Motohiro Tsubota and Dr. Kazuo Haga of Utsunomiya University for their helpful discussions.

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