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Synthesis and Characterization of Amphiphilic Polyisobutylene/Poly(Ethylene Glycol) Di- and Triblock Copolymers

1. Synthesis of Di- and Triblock Copolymers*

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Summary

Di- and triblock copolymers of polyisobutylene PIB and poly(ethylene glycol) PEG have been prepared and characterized. The syntheses involved the capping with tolylene 2,4-diisocyanate TDI various molecular weight α-phenyl-ω-(p-phenol)polyisobutylenes C_6H_5-PIB-C_6H_4OH and α,ω-di-(p-phenol)polyisobutylenes HOC_6H_4-PIB-C_6H_4OH, or commercially available mono- and di-hydroxyl-terminated PEGs. In this manner a series of PIB-b-PEG diblock copolymers, and PEG-b-PIB-b-PEG and PIB-b-PEG-b-PIB triblock copolymers have been obtained. The complete removal of the prepolymers from these amphiphilic sequential copolymers by conventional solvent extraction techniques could not be achieved because of the very high emulsifying action of the latters. In contrast, satisfactory separation was obtained by column chromatography using mixed (polar/nonpolar) eluents. The blocking efficiencies and composition of the block copolymers have been determined.

Introduction

Amphiphilic polymers, i.e., products that dissolve or swell in both aqueous and organic media, are of great interest for academic investigators as well as for a variety of applications in the cosmetic, pharmaceutical, detergent, coating, agricultural (1) and oil-recovery (2) industries. An important class of amphiphilic polymers are block or graft copolymers that contain a water-soluble and an organic solvent-soluble sequence. Typical representatives of such species are the commercially available poly(propylene oxide)/poly(ethylene oxide) block copolymers used as nonionic detergents in scores of applications.

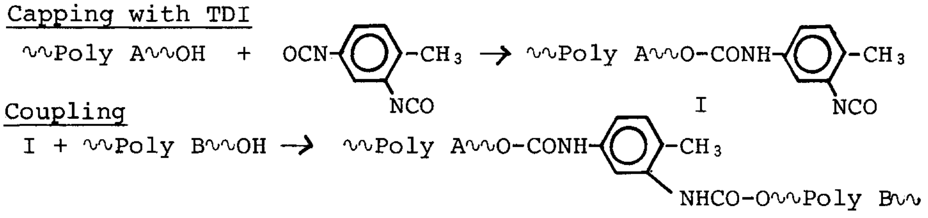
Recently a new class of well-defined telechelic polyisobutylenes PIB carrying one, two or three terminal functions became available (3,4).

We postulated that these PIBs would provide versatile inexpensive organic solvent-soluble segments which in combination with conventional water-soluble segments, e.g., PEG, would yield interesting new amphiphilic block copolymers. This

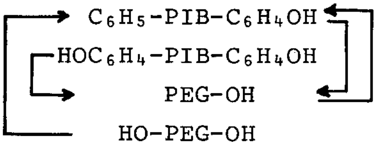
*Part XL V of the Series on "New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator-Transfer Agents (Inifers)".

series of papers describe the synthesis of various new PIB/PEG di- and triblock copolymers and their characterization by a variety of techniques.

The following scheme helps to visualize the possible synthesis routes:



where Poly A and Poly B are combinations of:



The combinations indicated by the arrows have been studied and the arrows point from the TDI-capped prepolymers toward the prepolymers used for coupling.

Experimental

Materials. The polymerization of isobutylene and other procedures (filtration, transfer, etc.) were carried out in a dry box under nitrogen (3). Benzene was distilled over a sodium dispersion and all reactions were carried out under anhydrous conditions.

Synthesis of α-phenyl-ω-(p-phenol)polyisobutylene and α,ω-di(p-phenol)polyisobutylene. The synthesis of HOC_6H_4-PIB-C_6H_4OH has been described (5). C_6H_5-PIB-C_6H_4OH was prepared by alkylation of phenol by α-phenyl-ω-isopropenylpolyisobutylene. In the present syntheses we used a 10 fold excess of phenol and equal moles of BF_3OEt_2 on the isopropenyl end groups of mono- or diisopropenylpolyisobutylene (5). After the reaction the hexanes (Fisher Scientific Co.) solution was washed by methanol and water, and poured into a large excess of acetone. The precipitate was fractionated from hexanes/methyl ethyl ketone mixture.

Synthesis of di- and triblock copolymers. C_6H_5-PIB-C_6H_4OH or HOC_6H_4-PIB-C_6H_4OH in benzene solution (5%) was dried over magnesium sulfate. The drying agent was filtered off in the dry box and to remove residual moisture ~1/3 of the benzene was removed (azeotropic distillation) under reduced pressure. The benzene solution was added dropwise to a TDI in benzene solution (1.2 - 1.5 times excess)at 45°C containing stannous octoate (2-3 drops) in a flask equipped with a magnetic stirring bar and a condenser.

PEG (Aldrich Chemical Co.) in benzene solution (10%) was dried over molecular sieves (3Å). The molecular sieves were filtered off in the dry box and a slight molar excess of the filtrate was added to the TDI-capped phenol-telechelic PIB in benzene solution. The solution was concentrated by removing some of the solvent under reduced pressure and the reaction mixture was stirred at 60°C for one day under anhydrous conditions.

Column chromatography. To separate the pure block copolymer the products were subjected to column chromatography. A column was packed by silica gel (Sargent-Welch Scientific Co.) and the crude product in benzene (10-20%) was passed through the column. The composition of the eluent was changed from nonpolar (hexanes) to polar (benzene/methanol) to obtain optimum separation and the filtrate was collected in several fractions.

The compositions of the isolated block copolymers were determined by ^{1}H-NMR spectroscopy. Blocking efficiency was estimated by IR spectroscopy or from the composition of the hexanes-extracted fraction.

Results and Discussion

Table I shows the molecular weights, molecular weight distributions, and number average end functionalities ($\overline{F}_n$) of C_6H_5-PIB-C_6H_4OH and HOC_6H_4-PIB-C_6H_4OH used in this work. M and B indicate mono- and bifunctional polymer, respectively, and the last number in the formula shows the molecular weight x 10^{-3}. For example, PIB-M-12 stands for a monofunctional PIB of $\overline{M}_n$ = 12,000.

Table I. Molecular Weights, Molecular Weight Distributions and Functionalities of α-phenyl-ω-(p-phenol)polyisobutylene and α,ω-di(p-phenol)polyisobutylene

Polymer	$\overline{M}_n$ [a]	$\overline{M}_w/\overline{M}_n$ [b]	$\overline{F}_n$ [c]
PIB-M-12	12,000	1.66	0.98 ± 0.07
PIB-M-5.5	5,500	1.32	1.03 ± 0.05
PIB-M-4.5	4,500	1.75	1.08 ± 0.06
PIB-M-2.8	2,800	1.27	1.09 ± 0.05
PIB-B-8.8	8,800	1.78	1.92 ± 0.10

a) by VPO b) by GPC c) by UV

The $\overline{F}_n$'s obtained are close to theoretical values i.e., $\overline{F}_n$ = 1 for monofunctional, and $\overline{F}_n$ = 2 for bifunctional polymers, indicating quantitative alkylation of phenol (5). The phenol ended PIBs were capped by TDI. The IR spectra of a representative sample before and after TDI capping are shown in Figure 1. After the reaction with TDI the absorption at 3650 cm^{-1} associated with phenolic OH groups disappeared and a new absorption corresponding to the NH stretching mode in the urethane linkage appeared. This indicates essentially complete capping of phenol end groups by TDI. The molecular weights of representative TDI capped PIBs were determined by GPC and they were essentially the same as those of the starting materials. Evidently chain extension is absent during capping.

Table II shows the molecular weights, molecular weight distributions and $\overline{F}_n$ of the commercial PEGs used.

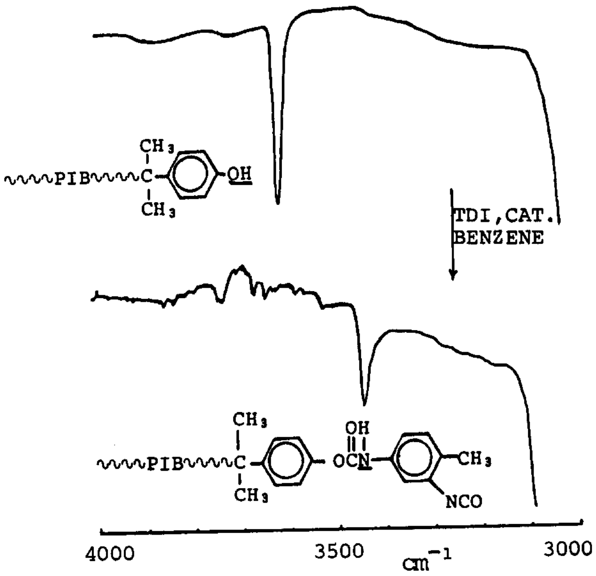


Figure 1. IR spectra of α-phenyl-ω(p-phenol)polyisobutylene and the product obtained after capping with TDI

Table II. Molecular Weights, Molecular Weight Distributions and Functionalities of Poly(ethylene glycols)

Polymer	$\overline{M}_n$ [a]	$\overline{M}_w/\overline{M}_n$ [b]	$\overline{F}_n$ [c]
PEG-M-5	5,000	1.05	1.11 ± 0.07
PEG-B-14	13,800	1.10	2.07 ± 0.11

a) by VPO b) by GPC c) by IR

The compositions, blocking efficiencies (B_{eff}) and molecular weights of representative block copolymers prepared in this research are listed in Table III.

Table III. Compositions, Blocking Efficiencies and Molecular Weights of PIB/PEG Block Copolymers

Block Polymers	B_{eff} (%)	Composition[a] (wt%) PIB	PEG	$\overline{M}_n$ [d] (g/mole)
PIB-M-12-b-PEG-M-5	-	74	26	23,000
PIB-M-4.5-b-PEG-M-5	75[b]	62	38	15,000
PIB-M-2.8-b-PEG-M-5	88[c]	24	76	6,900
PIB-M-5.5-b-PEG-B-14-b-PIB-M-5.5	85[c]	38	62	25,000
PEG-M-5-b-PIB-B-8.8-b-PEG-M-5	-	65	35	17,000

a) by H-NMR b) Solvent extraction by hexanes c) by IR
d) by composition and $\overline{M}_n$ of PEGs

The first three materials are diblock copolymers; the first two were prepared by coupling PEG-M-5 with TDI-capped monofunctional PIBs whereas the third one was obtained by coupling C_6H_5-PIB-C_6H_4OH with TDI-capped monofunctional PEG of M_n = 5000. The fourth and fifth entries were synthesized by first capping with TDI the prepolymer that was to provide the center block (i.e., HO-PEG-OH in the fourth and HOC_6H_4-PIB-C_6H_4OH in the fifth row) and subsequently coupling with the prepolymer of the outer block (i.e., C_6H_5-PIB-C_6H_4OH in the fourth and PEG-OH in the fifth row).

The compositions determined by ^{1}H-NMR spectra are different from the expected values due to unavoidable fractionation of different compositions by column chromatography i.e., the homo-PEG fraction contained PEG-rich block copolymer.

Figure 2 shows GPC traces of a representative diblock copolymer PIB-M-12-b-PEG-M-5 and those of the starting materials PIB-M-12 and PEG-M-5. The solid and dotted lines represent respectively the RI and UV responses. The RI trace of the crude product exhibits three peaks: the peak at highest elution count (lowest molecular weight) corresponds to PEG-M-5, the middle peak is due to self-coupled PEG, and the peak at the lowest elution count is due to the PIB-b-PEG block copolymer. Since a slight stoichiometric excess TDI was charged to the system to compensate for the presence of possible impurities (cf. Experimental), some free TDI must have remained in the system after capping. The residual TDI reacted with two moles of PEG and produced the self-coupled PEG (with a TDI unit in the middle), thus the molecular weight of the product is about twice that of the PEG used.

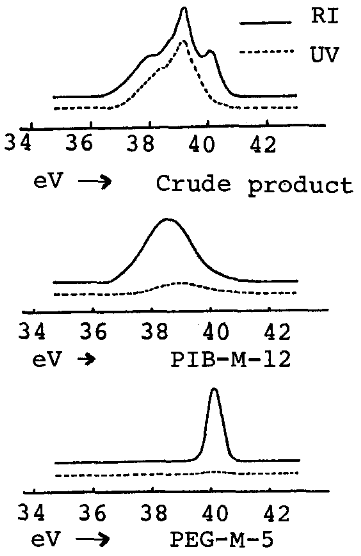
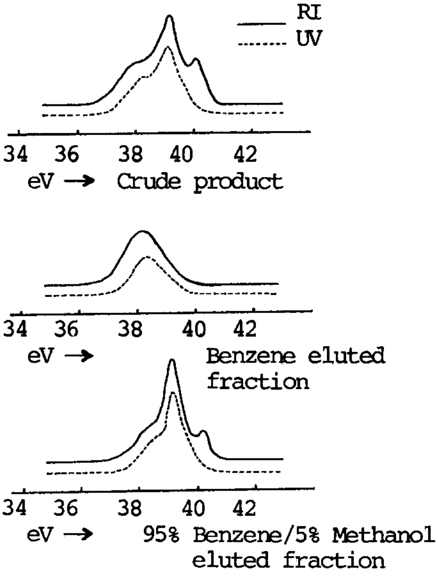


Figure 2. GPC chromatograms of reaction product and the original prepolymers (PIB-M-12-b-PEG-M-5)

The UV trace indicates the presence of a chromophore in the polymer. The PEG does not contain a chromophore and does not exhibit a UV response (the peak at highest elution count). In contrast, the block copolymer and the self-coupled PEG contain a phenyl urethane linkage and exhibit strong UV response.

Efforts have been made to purify the block copolymers by solvent extraction and/or precipitation techniques, however, all these procedures failed because of the extreme emulsifying activity of the amphiphilics. In contrast, satisfactory separations have been obtained by column chromatography. Figure 3 shows the GPC traces of a representative crude product, together with the benzene-eluted and 95% benzene/5% methanol-eluted fractions obtained by column chromatography. The benzene-eluted fraction gives a smooth unimodal GPC trace and does not show peaks corresponding to those of homopolymers (original or self-coupled PEG) indicating that this fraction does not contain homoPEG. By using a slightly more polar solvent mixture (95% benzene/5% methanol) homoPEG started to be eluted (cf. Figure 3). The GPC trace contains a peak at a lower elution count (higher molecular weight): this peak is eluted at a lower count than that of the original PIB indicating that it corresponds to the block copolymer. The fact that this block copolymer could not be eluted by benzene indicates that it is a PEG-rich block copolymer. Although the PEG-rich block copolymer could not be isolated (due to unavoidable fractionation by column chromatography), the low PEG content block copolymer (benzene-eluted fraction) was separated without appreciable homoPEG contamination.



Crude product

Benzene eluted fraction

95% Benzene/5% Methanol eluted fraction

Figure 3. Separation of amphiphilic block copolymer by column chromatography (silica gel) (PIB-M-12-b-PEG-M-5)

In the cases of the PEG-centered triblock copolymer and the long-PEG short-PIB diblock copolymer i.e., entries four and three in Table III, homoPIB was first eluted by benzene and the block copolymer was obtained by washing the column with a benzene/methanol mixture that contained 30-50% methanol.

Efforts have been made to determine the molecular weights of the block copolymers by VPO, however, due to the purification difficulties (presence of trace amounts of solvent) reliable values could not be obtained. Thus, block copolymer molecular weights were estimated from compositions obtained by ^{1}H-NMR spectroscopy and the molecular weight of the PEG segment. Since the molecular weight distributions of the PEGs are very narrow ($\bar{M}_w/\bar{M}_n < 1.10$), the molecular weights of PEG segments in the block copolymers were assumed to be identical to those of the original PEGs.

Blocking efficienty, i.e., the percent of TDI capped polymer incorporated in the block copolymer, was estimated by IR or ^{1}H-NMR spectroscopy. In the cases of PIB-M-2.8-b-PEG-M-5 and PIB-M-5.5-b-PEG-B-14-b-PIB-M-5.5 the concentration of free phenolic OH groups was determined by IR spectroscopy employing very low sample concentrations ($\sim 10^{-4}$ mole/ℓ in CCl_4). Based on the amount of free OH and known amounts of PIB, TDI and PEG charged, the blocking efficiencies could be calculated. In the case of PIB-M-4.5-b-PEG-M-5, solvent extraction by hexanes was carried out and the amount of homoPIB was determined by subtracting the amount of the block copolymer from the total amount of the hexanes-soluble fraction. The amount of the block copolymer in the hexanes-soluble fraction was calculated from the composition of the hexanes-soluble fraction and assuming that the PEG is incorporated in the block copolymer and that the composition of the block copolymer is the expected value i.e., the PIB/PEG weight ratio is 4.5/5. In both cases, minimum values are obtained because the presence of impurities (such as water) will reduce the value in the former cases, and the real PIB content in the block copolymer should be higher than the expected value in the latter case. Thus, the blocking efficiencies in these systems were found to be higher than 80%.

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