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

2. Characterization of Polyisobutylene/Poly(Ethylene Glycol) Diblock Copolymers*

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Summary

Poly(isobutylene-b-ethylene glycol) PIB-b-PEG diblock copolymers have been synthesized by reacting tolylene 2,4-diisocyanate-capped polyisobutylene with monohydroxyl-ended poly(ethylene glycol). The block copolymers form stable benzene-water emulsions and show surface activity decrease in interfacial surface tension, and existence of critical micelle concentration. Turbidimetry of the block copolymers indicates the expected wide range of solubility from nonpolar to polar solvents. The temperature dependence of the intrinsic viscosity of the block copolymers exhibits characteristic discontinuities. The intrinsic viscosity of the block copolymer as a function of solvent polarity was studied and the observations were explained as the sum of segment contributions based on the "segregated" conformation model. DSC also indicates microphase separation in the solid state due to segment incompatibility.

Introduction

Amphiphilic polymers dissolve or swell in both organic and aqueous media and are of great interest because of their unique emulsifying, thickening, foaming, etc. properties. Nonionic surfactants consist of a water-soluble and a water-insoluble moiety, and are typical of commercially available aphiphilic polymers.

Recently well-defined telechelic PIBs became available(1) and amphiphilic block copolymers based on PIBs were prepared by the combination with a conventional water-soluble segment, e.g., PEG (2). In this paper, these new amphiphilic block copolymers are characterized by a variety of techniques such as DSC, surface tension measurement, turbidimetry, and intrinsic viscosity measurement.

Experimental

Synthesis of poly(isobutylene-b-ethylene glycol).

Synthesis of the prepolymer, α-phenyl-ω-(p-phenol)polyisobutylene, C_6H_5-PIB-C_6H_4OH and PIB-b-PEG diblock copolymers, together with separation techniques and composition determinations have been described (2).

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

Surface tension. Interfacial surface tension was measured by a Fisher Surface Tensiometer Model 20. The surface tension at benzene/water interface was obtained as a force which is required to release the platinum ring from the interface. The surface tensions were measured and plotted at different concentrations.

DSC. Thermal behavior of PIB-b-PEG was examined by a DuPont Thermal Analysis Instrument 1090. The sample (20 mg) was placed in an aluminum dish and the DSC measurement was carried out at 10°C/min heating rate from -100°C to + 100°C.

Turbidimetry. Polymers in toluene solution (0.3%) were prepared in Erlenmeyer flasks, and methanol or hexanes was slowly added from a buret. The absorbance after each nonsolvent addition was determined (Beckman Model 25 Spectrophotometer at 700 nm) and plotted against the amount of the nonsolvent added.

Viscosity. Relative viscosities were obtained by an Ubbelohde viscometer in a constant temperature water bath. The intrinsic viscosity was determined by extrapolation to concentration C = 0 of the plot of the specific viscosity η_{sp}/C against C. The intrinsic viscosity of block copolymers was determined in toluene at different temperatures from 25 to 45°C, or at 25°C in solvent mixtures with different compositions (toluene/hexanes or toluene/methanol).

Results and Discussion

The compositions and molecular weights of PIB-b-PEGs are listed in Table I.

Table I. Compositions and Molecular Weights of the Block Copolymers

Block Polymers[a]	Composition[b] (wt%)		$\bar{M}_n$ [c] (g/mole)
	PIB	PEG	
PIB-M-12-b-PEG-M-5	74	26	23,000
PIB-M-4.5-b-PEG-M-5	62	38	15,000
PIB-M-2.8-b-PEG-M-5	24	76	6,900

a) Abbreviations defined in the previous paper of this series
b) by ^{1}H-NMR
c) by composition and $\bar{M}_n$ of PEG-M-5

Preliminary investigations indicated a very high emulsifying activity of PIB-b-PEG block copolymers. For example, stable emulsions have been obtained by shaking benzene solutions of block copolymers (3wt%) with an equal volume of water at room temperature; no phase separation after several days of storage at room temperature was noticeable. Subsequently experiments have been carried out to define in some detail surface activity of these new materials.

Interfacial Surface Tension Measurements. The interfacial surface tension of PIB-M-12-b-PEG-M-5 in dilute benzene solution ($\sim 10^{-5}$ mole/ℓ) at a water/benzene interface was measured and plotted against the concentration. Figure 1 shows the interfacial surface tension/concentration plot. The surface tension decreases with the concentration of the block copolymer and after a certain concentration it becomes constant. This behavior is typical of surface active materials at an interface and the concentration at which the surface active material is saturated at the interface is called critical micelle concentration (CMC). This particular PIB-b-PEG shows a CMC at $\sim 3.0 \times 10^{-5}$ mole/ℓ which is a reasonable value for a long chain nonionic surfactant (3).

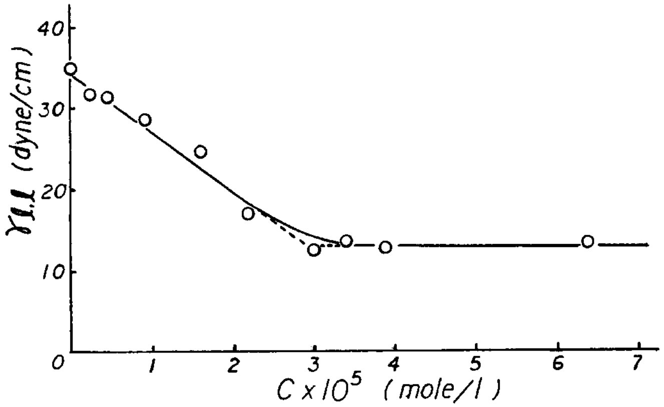

Figure 1. Interfacial Surface Tension of PIB-M-12-b-PEG-M-5 (benzene/water)

Turbidimetry. Figure 2 shows the results of a series of turbidimetry measurements of the block copolymers together with those of the original prepolymers. The turbidity of the block copolymers appears at higher amounts of nonsolvent than those of the prepolymers because one of the segments (PEG in the case methanol is added, PIB in the case hexanes is added) enhances the solubility of the block copolymer in the particular solvent mixture. This finding suggests the absence of homopolymers in the block copolymer systems.

Significantly, the intensity of the turbidity of the block copolymers increases only to a very small extent as compared to that of the homopolymers. (The relatively high turbidity observed with the block copolymer PIB-M-2.8-b-PEG-M-5 is undoubtedly due to the very short PIB segment in the system.) The block copolymers form stable micelles and the turbidity is due to the micelles, not to precipitated coils.

DSC Studies. Figure 3 shows DSC traces of representative PIB-b-PEGs. The traces clearly exhibit a glass transition temperature (Tg) and a melting point (mp) corresponding to the PIB and PEG segments respectively. These data indicate microphase separation in the solid state due to a high degree of incompatibility of the segments.

Dilute Solution Properties

The Effect of Temperature. The dilute solution behavior of PIB-b-PEGs has been investigated by intrinsic viscosity [η] studies. The effect of temperature on [η] has been observed to change in a characteristic manner for sequential copolymers. For example, butyl rubber-g-polytetrahydrofuran

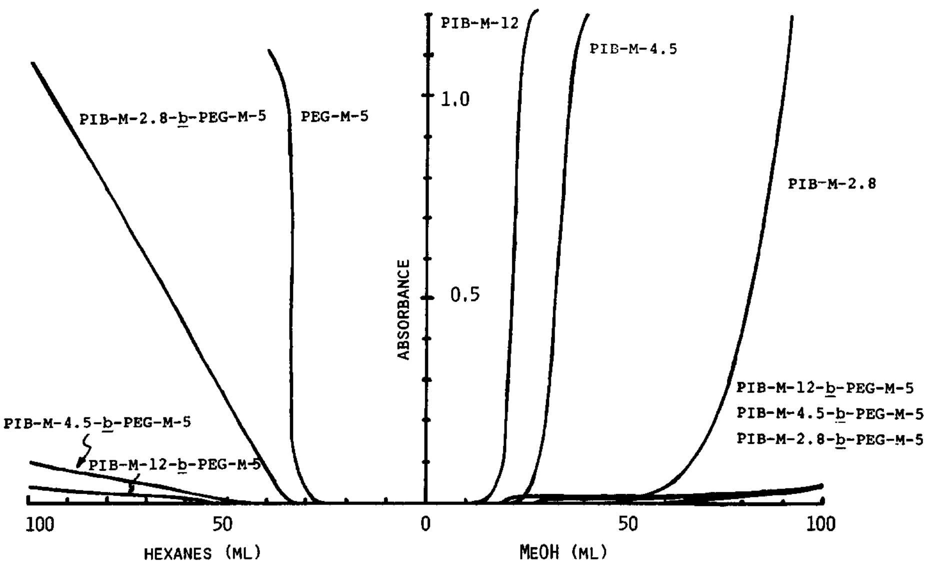

Figure 2. Turbidimetry of PIB-b-PEG Block Copolymers (in toluene)

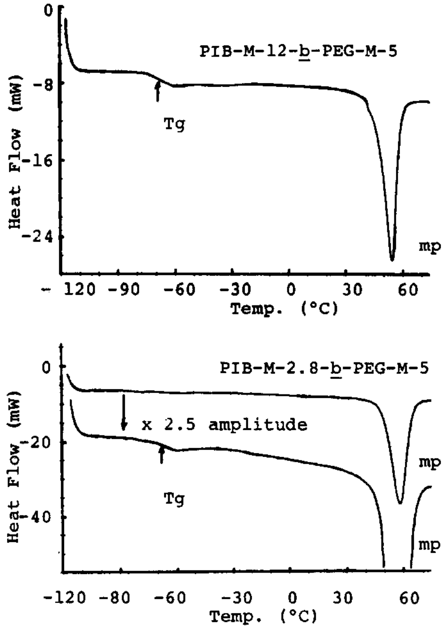

Figure 3. DSC Traces of PIB-b-PEG Block Copolymers

PTHF (4) and PTHF-b-PIB-b-PTHF (5) show distinct changes in the slope (sign) of [η] versus temperature plots in toluene solvent. We have also investigated the [η] versus temperature profile of PIB-b-PEGs in toluene in the temperature range from 25° to 45°C. Figure 4 shows the observations. The discontinuity observed with all three block copolymers is strong evidence for the presence of a highly phase-separated system. The first ascending branch of the [η] versus temperature plot (from ∿25° to ∿28°C) indicates an increase in the hydrodynamic volume; over the second region from ∿28° to ∿35°C the hydrodynamic volume of the block copolymer system decreases due to possible segment mixing. Finally over the range from ∿35°C to ∿45°C the hydrodynamic volume starts to rise again. Only sequential (block and/or graft) copolymers exhibit such a characteristic [η] versus temperature profile (4,5).

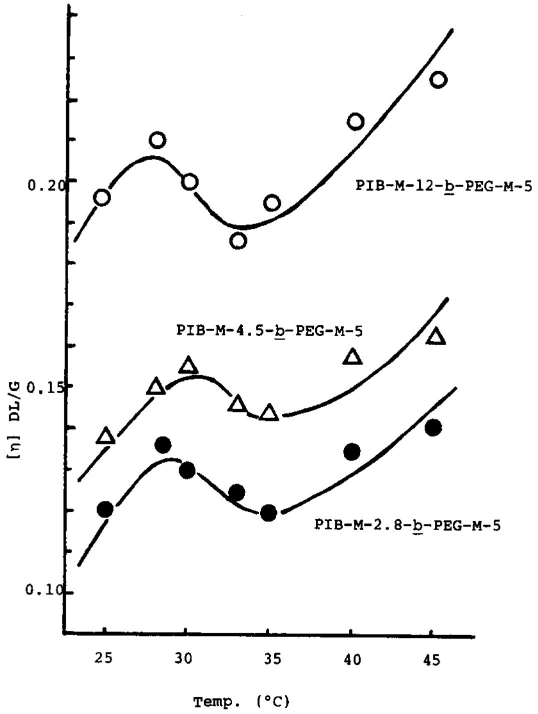

Figure 4. Temperature Dependence of Intrinsic Viscosity of PIB-b-PEG Block Copolymers (in toluene)

The Effect of Solvents. Next we investigated the effect of the nature of solvent mixtures on the intrinsic viscosity of PIB-b-PEGs. Figure 5 shows the results of a series of representative experiments. We prepared a series of hexanes/toluene and methanol/toluene mixtures of various compositions. In these mixtures toluene is a solvent for both contributing segments whereas the hexanes and methanol are dissolving only one of the constituents (i.e., hexanes is a solvent for PIB and methanol for PEG). Subsequently we dissolved a block copolymer, PIB-M-12-b-PEG-M-5, and the two prepolymers PIB-M-12 and PEG-M-5 in this series of solvent systems, and determined their intrinsic viscosities at 25°C. Figure 5 shows the data. The block copolymer could be dissolved over the entire solvent composition regime, although the system becomes hazy over ∿50 ml hexanes and over ∿15 ml methanol in the solvent mixture. The detailed features of the [η] versus solvent composition curve are difficult to explain (for example, the sharp maximum at ∿5 ml methanol). In contrast, the PEG-M-5 and PIB-M-12 prepolymers could not be dissolved in a mixture that contained more than 10 ml hexanes and 10 ml methanol, respectively. These data most likely reflect a complex series of conformational changes due to the presence of intrinsically segregated phases in a liquid whose composition is continuously changing.

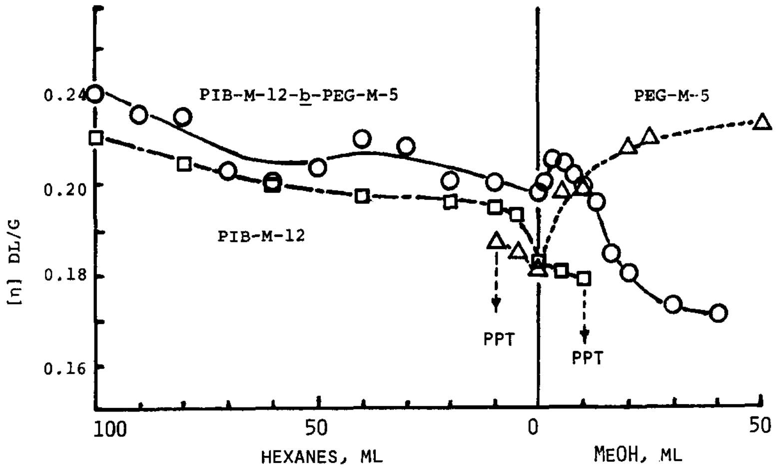

Figure 5. Intrinsic Viscosity as a Function of Solvent Polarity (PIB-M-12-b-PEG-M-5)

Semiquantitative Application of the "Segregated" Model. The segregated model has been proposed to describe the poly(methyl methacrylate-b-styrene) system and the intrinsic viscosities calculated based on the model from the sum of the intrinsic viscosities of the contributing segments have been found to be very close to those of experimental values (6). A similar calculation was carried out with our PIB-b-PEGs. The intrinsic viscosity is expressed as shown in equation (1) (7).

$$[\eta] = \Phi V_e / M \tag{1}$$

where Φ is a constant which appears to be the same for all polymer coils, M is the molecular weight, and V_e is the effective hydrodynamic volume. Hence

$$V_{e,PIB} = [\eta]_{PIB} \cdot M_{PIB}/\Phi \tag{2}$$

$$V_{e,PEG} = [\eta]_{PEG} \cdot M_{PEG}/\Phi \tag{3}$$

Based on the segregated model, $V_{e,block}$ should be the sum of $V_{e,PIB}$ and $V_{e,PEG}$.

Thus

$$V_{e,block} = ([\eta]_{PIB} \cdot M_{PIB} + [\eta]_{PEG} \cdot M_{PEG})/\Phi \tag{4}$$

$$\begin{aligned} [\eta]_{block} &= \Phi V_{e,block}/M_{block} \\ &= ([\eta]_{PIB} \cdot M_{PIB} + [\eta]_{PEG} \cdot M_{PEG})/M_{block} \end{aligned} \tag{5}$$

$[\eta]_{PIB}$ was calculated from the relationship $[\eta] = k'M^a$ ($K = 87 \times 10^{-5}$, $a = 0.56$), because the molecular weights of the PIB segments are different from those of the original PIBs (fractionation due to column chromatography). $[\eta]_{PEG}$ was experimentally obtained and M_{PEG} is the same as that of the original PEG. Table II shows the calculated values together with experimental values.

Table II. Experimental and Theoretical Intrinsic Viscosities

Block Polymers	[η] in toluene at 25°C (g/dl)	
	Theoretical	Experimental
PIB-M-12-b-PEG-M-5	0.199	0.196
PIB-M-4.5-b-PEG-M-5	0.154	0.138
PIB-M-2.8-b-PEG-M-5	0.132	0.120

According to our calculation the theoretical values are very close to the experimental ones. In light of these findings the block copolymers are in a segregated conformation in solution which is in agreement with the notion of segment incompatibility expected for these block copolymers.

Conclusion

According to these investigations, including the solid phase and dilute solution characterization of PIB-b-PEG block copolymers, these materials exist in a highly segregated conformation (phase separated state) both in the solid and liquid phase, and exhibit pronounced amphiphilic character. As such, these materials should be of interest for a variety of applications in the detergent, cosmetic, oil-recovery, polymer-blending etc. industries.

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