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## Block Polymers Derived from Poly(ethylene Oxide) and Poly-3,3-dimethylthietane

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### ABSTRACT

Poly(ethylene oxide-*b*-3,3-dimethylthietane) was prepared by coupling of preformed poly-3,3-dimethylthietane (PDMT) with poly(ethylene oxide) (PEO). PDMT was endcapped with 2,4-toluene diisocyanate (TDI) and then reacted with molar excess of PEO. AB type block polymers were obtained. Absorption by complexation of silver nitrate and iodine by these block polymers was investigated. It was found that the presence of the PEO segment in the block polymer was essential for complexation. Iodine absorption was not accompanied by other side reactions leading to chain scission of the polysulfide, as was found with poly(propylene sulfide).

### INTRODUCTION

Block polymers of poly-3,3-dimethylthietane (PDMT) and vinyl or diene polymers can be prepared by anionic [1] and cationic [2] polymerization from the corresponding monomers. These block polymers are composed of two hydrophobic segments. Block polymers of PDMT

containing a hydrophilic segment such as poly(ethylene oxide) (PEO) may be of interest. Such block polymers may be used for absorption by complexation of halogens and heavy metal salts. It was already reported [3, 4] that poly(propylene sulfide) (PPS) and poly(ethylene sulfide) (PES) grafted on a hydrophilic polymer, such as cellulose, can be used for this purpose. It was found that silver, mercury, and other heavy metal salts as well as iodine could be absorbed by cotton fabrics and cellulosic films grafted with the corresponding episulfide. Almost complete participation of the sulfide groups in the complexation reaction was achieved. Iodine absorption was accompanied by degradation reaction leading to scission of the grafted side chains. It was suggested [3] that chain scission was the result of iodine substitution of the PPS or PES backbone. Such backbone-substituted iodine is always  $\beta$  to the sulfide group, easily hydrolyzed by water to an  $\alpha$ -hydroxy sulfide which in turn is unstable and can hydrolyze with rupture of the sulfide bond.

It was of interest to find out whether block polymers of PDMT can be used for absorption by complexation of silver nitrate and iodine. If a chain scission reaction does not occur with this polymer, there may be an advantage in using PDMT block polymers for absorption of iodine.

The possible use of preformed polymers for the synthesis of poly(ethylene oxide-*b*-3,3-dimethylthietane) was investigated. Hydroxy-terminated PEO is commercially available. PDMT can be easily prepared by cationic polymerization [5-8] of DMT. Successful polymerization of this monomer with boron trifluoride etherate was already reported [5]. It is expected that the boron trifluoride initiated PDMT will contain a terminal mercaptan group. Endcapping of this mercaptan-terminated PDMT with 2,4-toluene diisocyanate (TDI), followed by reaction with hydroxy-terminated PEO, will lead to the desired block polymer.

## EXPERIMENTAL

### Materials

PEO, TDI (80/20 mixture of 2,4- and 2,6-isomers) (Fluka) and methylene chloride (Frutarom) were used. Boron trifluoride etherate (Fluka) was distilled over calcium hydride before use [9]. Tetrahydrofuran (THF) was dried by distillation from sodium benzophenone before use. 3,3-Dimethylthietane (DMT) was prepared by a method previously reported [12].

### Polymerization of DMT

The procedure reported in the literature [5] was adapted. DMT was polymerized by boron trifluoride etherate in methylene chloride. The methylene chloride was removed under vacuum and the crude polymer was triturated in methanol several times before isolation. Molecular weight was determined by the melting point depression method [11] with carbon tetrabromide.

### Block Polymerization

A typical procedure is described. PDMT (1.0 g, MW 2150) was allowed to react with TDI (0.13 ml) in the presence of dibutyltin dilaurate (0.05 ml) in methylene chloride (50 ml) for 24 hr at room temperature. PEO (1.0 g, MW 1000) in THF (50 ml) was added. The reaction mixture was allowed to stand at room temperature for 24 hr. Reaction solvent was removed under vacuum, and the crude polymer was extracted with methanol (75 ml) for 3 days.

### Absorption Experiments

Block polymers were kept in 0.1 N iodine or 0.1 N silver nitrate solution in water at room temperature for the required length of time. The total amount of iodine removed from solution was determined by titrating an aliquot of this solution with 0.1 N sodium thio-sulfate. The amount of complexed iodine was calculated from titration of the complexed iodine together with the iodine left in solution. The amount of complexed silver nitrate was determined by titration of an aliquot of the silver nitrate solution with 0.1 N ammonium thio-cyanate.

### Reaction of PDMT and PPS with Iodine

To PDMT (0.2 g) in THF (50 ml) containing 4% water, iodine (0.381 g) was added. Similarly iodine (0.254 g) was added to PPS (0.1 g) in THF (50 ml) containing 4% water. The sample of the reaction mixture was immediately transferred to an Ubbelohde viscometer and was kept at 25°C.

## RESULTS AND DISCUSSION

Block polymerization of preformed PDMT and PEO was investigated. Commercially available PEO was used. PDMT was prepared by

TABLE 1. Reaction of Isocyanate-Terminated PDMT with PEO<sup>a</sup>

PDMT MW	PDMT <sup>b</sup> PEO	Block Polymer Analysis		PEO in the Block polymer (%) <sup>c</sup>	Unextracted PDMT (%) <sup>d</sup>	PEO <sup>e</sup> PDMT
		N (%)	S (%)			
1810	0.33	4.0	16.5	23.8	84.0	1.14
2150	0.47	1.7	22.3	20.7	44.4	0.95
2150	0.37	0.9	20.9	29.7	97.1	0.97
2150	0.48	1.0	21.7	26.6	96.2	0.92

<sup>a</sup>PDMT in methylene chloride (50 ml) was allowed to react with equimolar amount of TDI in the presence of dibutyltin dilaurate (0.05 ml) for 24 hr. PEO (MW 1000) in THF (20 ml) was added. The reaction mixture was kept at room temperature for 24 hr. The crude reaction product was extracted with methanol.

<sup>b</sup>Reactants molar ratio.

<sup>c</sup>Calculated from block polymer analysis and corresponds to the methanol insoluble fraction.

<sup>d</sup>% of the PDMT used.

<sup>e</sup>Molar ratio of the PEO in the block polymer to unextracted PDMT.

polymerization of DMT with boron trifluoride. PDMT was first endcapped with 2,4-TDI. Endcapping was carried out in the presence of dibutyltin dilaurate, which served later as a catalyst for the block polymerization reaction. Since reaction of isocyanate with a mercaptan is usually slower than that with a primary hydroxyl group, a long reaction time was allowed for the endcapping reaction. The preparation of poly(ethylene oxide-*b*-3,3 dimethylthietane) from isocyanate terminated PDMT and PEO is reported in Table 1. The isocyanate-terminated PDMT was prepared by reaction of equimolar amounts of PDMT with TDI. In all experiments, a molar excess of PEO (1,000 MW) was used. Unreacted PEO was removed by extraction with methanol. All the PEO present in the methanol insoluble fraction was incorporated in the block polymer. The isolated block polymer may contain some PDMT homopolymer also. Due to similarity in solubility properties between the block polymers obtained and PDMT, the unreacted PDMT could not be removed, and complete separation between unreacted preformed polymers and the derived

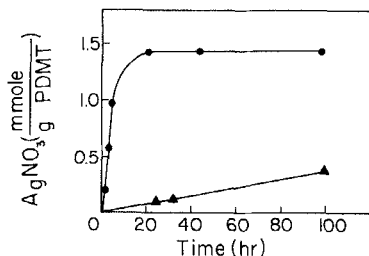


FIG. 1. Absorption of silver nitrate by poly(ethylene oxide-*b*-3,3-dimethylthietane): (●) block polymer of 36.4% PEO content; (▲) PDMT homopolymer. Absorption was carried out in 0.1 N silver nitrate solution at molar ratio Ag/S = 2.

block polymer was not feasible. Nevertheless, the molar ratio of PEO which was incorporated in the block polymer and was found in the methanol-insoluble block polymer to PDMT in this main fraction indicates the formation of an AB type polymer in a very good yield. Most of the PDMT reacted and was incorporated in the block polymer.

The block polymers prepared contained also a small methanol-soluble fraction. The unreacted PEO which was extracted by methanol contained 3-7% of PDMT which, as a homopolymer, is methanol-insoluble.

The incorporation of a segment containing sulfide groups in the block polymer may render it useful for absorption by complexation of halogens and heavy metal salts. Absorption of silver nitrate from aqueous solution by poly(ethylene oxide-*b*-3,3 dimethylthietane) was investigated. Absorption by complexation was carried in 0.1 N silver nitrate solution with the use of a molar excess of silver salt. Time dependence of complexation reaction is described in Fig. 1. Complexation was completed after 24 hr. It can be seen that the extent of complexation of PDMT in the block polymer is much higher than that of PDMT homopolymer. The presence of the PEO segment is essential for the participation of the PDMT in complexation reaction. Increase in the hydrophilic segment content of the block polymer led to an increase in absorption by complexation of silver nitrate from water solution (Table 2). When block polymer of 74.4% PEO was used, 40% of the sulfide groups participated in complexation.

The presence of block polymer could also improve complexation by the homo PDMT itself. When block polymer was added to PDMT homopolymer, an increase in extent of complexation by the PDMT was observed. A mixture containing 16.7% PEO was prepared from PDMT homopolymer and block polymer of 53.6% PEO content. The mixture

TABLE 2. Absorption of Silver Nitrated by Block Polymers of Different PEO Content<sup>a</sup>

PEO in the block polymer (%)	Complexed silver nitrate <sup>b</sup>	
	(mmole/g PDMT)	Ag/S <sup>c</sup>
0.0 <sup>d</sup>	0.10	0.01
16.0	0.10	0.01
36.4	1.47	0.15
74.4	3.91	0.40

<sup>a</sup>Block polymer (1.0 g) was kept in 0.1 N silver nitrate solution at room temperature for 24 hr. Molar excess of silver nitrate (Ag/S = 2), was used.

<sup>b</sup>Determined by titration.

<sup>c</sup>Molar ratio in the block polymer.

<sup>d</sup>PDMT homopolymer.

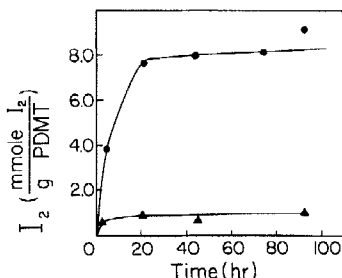


FIG. 2. Absorption of iodine by poly(ethylene oxide-b-3,3-dimethylthietane): (●) block polymer of 36.4% PEO content; (▲) PDMT homopolymer. Absorption was carried out in 0.1 N iodine solution at molar ratio  $I_2/S = 1$ .

of these two components was prepared by evaporation of their THF solution to dryness. The mixture was left in 0.1 N silver nitrate solution using experimental conditions as those reported in Table 2. It was found that 2.64 mmole/g PDMT of silver nitrate, corresponding to an Ag/S molar ratio of 0.27, was absorbed. This value could not be attributed only to absorption by the PDMT in the block polymer,

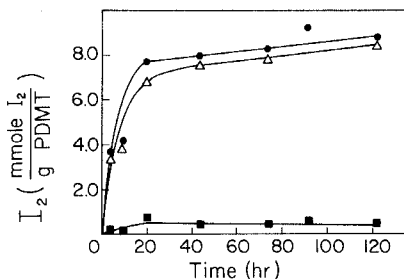


FIG. 3. Reaction and complexation of iodine with poly(ethylene oxide-b-3,3dimethylthietane): (●) iodine removed from solution; (△) complexed iodine; (■) reacted iodine. Absorption was carried out in 0.1 N iodine solution at molar ratio  $I_2/S = 1$ . Block polymer of 36.4% PEO content was used.

since it will correspond to an Ag/S molar ratio of 1.71. The presence of PEO facilitated diffusion of silver nitrate and its complexation by both block polymer and PDMT homopolymer.

Absorption of iodine by the block polymer was carried in aqueous solution. Absorption was completed after 20 hr (Fig. 2). Here, too, the presence of the PEO segment is essential. The value of 7.7 mmole/g PDMT iodine absorbed by the block polymer corresponds to participation of 90% of the sulfide groups in reaction. Under the same experimental conditions, when PDMT homopolymer was used, only 9% of these groups reacted. The complexed iodine could be titrated by thiosulfate. It was found that more than 95% of the iodine removed from solution by the block polymer was complexed by PDMT in the block polymer and could be titrated (Fig. 3). When absorption was completed, the extent of complexation did not change with reaction time. Different behavior was reported for cellulose-g-poly(propylene sulfide) [3]. Absorption of iodine by the grafted PPS was accompanied by substitution reaction, about 50% of the iodine removed from solution reacted with the grafted PPS and could not be titrated by sodium thiosulfate. Complexation of the iodine by the grafted PPS was accompanied by degradation which led to scission of the grafted PPS.

It was suggested [3] that chain-substituted iodine facilitated these degradation reactions. Chain-substituted iodine is always  $\beta$  to a sulfide group; since  $\beta$ -halosulfides are known to undergo rapid hydrolysis [12] via an episulfonium ion, hydrolysis leading to chain scission took place.

Any degradation leading to chain scission should be detected by



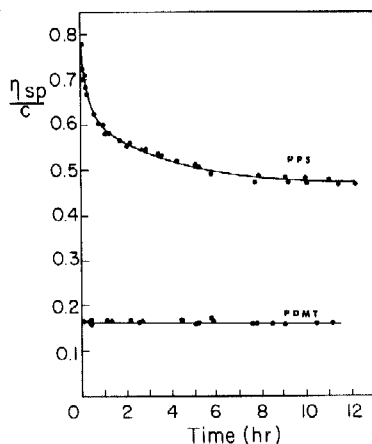


FIG. 4. Change in solution viscosity in reaction of iodine with PDMT and PPS.

decrease in viscosity of the reaction mixture. PPS and PDMT were allowed to react with iodine in THF in the presence of 4% water. Reaction was carried out in the presence of molar excess of iodine. The change in viscosity of the reaction solution with time was followed (Fig. 4). A decrease in PPS solution viscosity was found, while no change in PDMT solution viscosity was observed during that time. Extent of reaction of iodine with PDMT was always low (Fig. 3), and since the  $\beta$  carbon atom in PDMT is already substituted, no substitution by iodine which will lead to chain scission could take place. Thus no degradation reaction accompanied complexation of iodine by PDMT.

It can be seen that there is an advantage in the use of PDMT over PPS for absorption by complexation of iodine. When block polymers of PDMT are used, practically all the iodine absorbed by the PDMT is complexed, and side reactions leading to decrease in extent of complexation and to chain scission are eliminated.

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