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Polymeric Reagents. III. Synthesis of an Insoluble Polymeric Thioanisole and Its Utilization for the Oxidation of Alcohols

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Abstract: Macroreticular cross-linked polystyrene (Ⓟ-C_6H_5) has been functionalized by substituting varying percentages of the aromatic rings with *p*-methyl sulfide groups. This polymer is an effective coreactant for the sulfide-based oxidation of primary and secondary alcohols. The reaction has also been extended to the selective monooxidation of 1,7-heptanediol.

Insoluble polymers as supports for reagents useful in organic synthesis have been receiving considerable attention since R. B. Merrifield[2] first reported the synthesis of polypeptides on a cross-linked polystyrene support. The advantages of the use of polymeric reagents in general organic syntheses have been described and exploited in a number of papers[3] and recently summarized by Overberger.[4]

Major advantages of this approach that have not previously been stressed are: (a) the possibility of reducing the potential of pollution stemming from chemical research and industrial chemical processes; and (b) the production of recyclable polymeric reagents, which would be of value to an industry facing inevitable scarcity of products.

Taking into account the above factors, we investigated the application of a polymeric thioanisole in the new Corey[5] oxidation method. Although many new and efficient methods to oxidize alcohols to aldehydes or ketones have been developed, the sulfide-based method is significant for its ease of operation, mildness of conditions, and low cost of reagents. However, a number of major disadvantages arise, particularly when one might want to apply this approach to an industrial process. These disadvantages include the noxious odor associated with dimethyl sulfide or thioanisole and the difficulty involved in removing thioanisole from many products. It is anticipated that a polymeric reagent, equivalent in function to the monomeric sulfides, could solve these disadvantages in addition to being reusable and simple to apply.

Our efforts have been directed toward the synthesis of the cross-linked polymeric sulfide **3**. Soluble *p*-methylmercaptostyrene has been prepared via the direct polymerization of the monomer.[6] Although this polymer would probably function in the oxidation process, it does not have all the desired properties that a cross-linked chain would provide. We chose to concentrate on the functionalization of macroreticular polystyrene.[7,8] A major consideration in use of a macroreticular resin is the macroporosity and rigidity[8] of the beads that give certain advantages over the ordinary gel-type polymers: its easy filtration, its nominal shrinking and swelling properties in the reaction solvents even with changing temperatures, and its more accessible reactive sites.

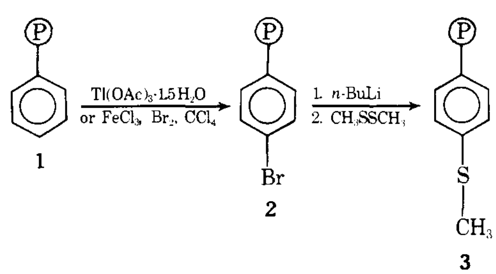


Table I. Oxidation of Alcohols with the Polymeric Sulfide Reagent 3 and Chlorine

Alcohol	Sulfide, equiv	Reaction time, hr	% yield GLC	% yield Isolated
1-Octanol	3.56	3	98	95[a]
PG alcohol 6	5.3	4		100[b]
4-Phenylcyclohexanol	3.56	4		90
Benzyl alcohol	3.30	5	66.7[c]	53[d]
3-(*p*-methoxyphenyl)-propan-1-ol	5.0	4		94[e]

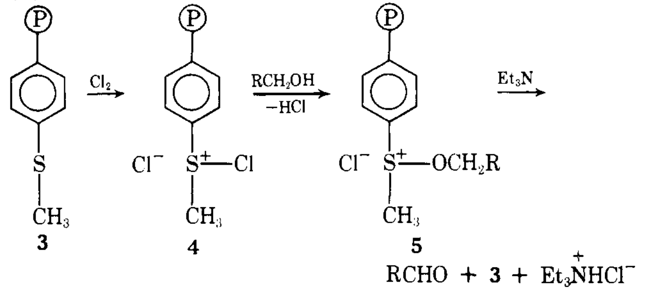
[a] 95% yield of distilled material of 97% purity. [b] Quantitative yield of material of approximately 90% purity based on NMR integration. [c] Benzyl chloride (33%) was also formed in this reaction. [d] Isolated as 2,4-DNP derivatives. [e] Yield for distilled material of 98.4% purity by GLC.

Macroreticular polystyrene, Ⓟ-C$_6$H$_5$, Amberlite XE-305 (Rohm & Haas),[9] was brominated in the presence of thallic acetate sesquihydrate [Tl(OAc)$_3$·1.5H$_2$O] in carbon tetrachloride[10] to yield polymer **2** containing 3.56 mmol of bromine per gram[11] of beads. Alternatively, the bromination of polystyrene **1** could be accomplished with bromine in CCl$_4$ using ferric chloride as catalyst.[12] In this case, the incorporation of 3.61 mmol per gram[11] of beads was obtained. The partially brominated beads **2** were treated with excess *n*-butyllithium in THF followed by methyl disulfide[13] to afford poly(*p*-methylmercaptostyrene) **3**. The sulfur content of **3** was 3.56 mmol per gram of the resin and could be adjusted as desired, simply by varying the amount of methyl disulfide, indicating a quantitative reaction between the lithiated polymer and methyl disulfide. The beads retained most of their physical and mechanical properties throughout the synthetic sequence.

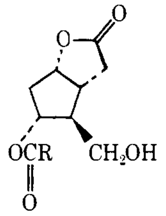
The polymeric sulfide **3** proved to be an effective replacement for thioanisole employed in the Corey oxidation method[5] of primary and secondary alcohols. The main advantages of use of this polymer are, as previously described: (1) the ease of work-up that allows convenient separation of the product from the oxidizing agent; (2) the polymer is free of odor so that it is suitable for industrial operation; and (3) the polymer can be reused[14] after washing since it does not change chemically during the reaction.

The yields of aldehydes and ketones from the oxidation of alcohols using the complex **4** from polymeric sulfide **3** and chlorine (Scheme I) were nearly equivalent to those of the monomeric sulfide-based oxidation methods.[5] However, longer reaction times were required with the polymer than with monomeric sulfides.

Scheme I



This oxidation technique has been found to be useful in dealing with highly sensitive compounds. Specifically the key prostaglandin intermediate[5b] **6** was readily converted to the desired labile aldehyde **7**. The results of oxidation of a series of alcohols using the polymeric sulfide and chlorine as coreactants are shown in Table I.



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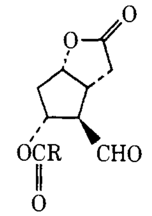

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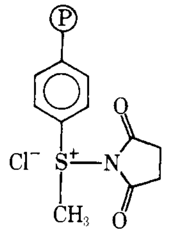

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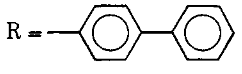
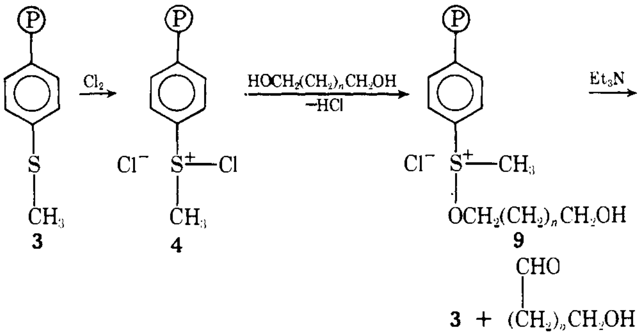


When the complex **8** from polymeric reagent **3** and *N*-chlorosuccinimide was used as the intermediate[5] in the oxidation process, the conversion of 1-octanol to octanal was found to be poor because of the competing formation of octyl chloride. The percentage of halide formed is strongly dependent on solvent polarity as indicated by the results displayed in Table II.

The monooxidation of difunctionalized alcohols would appear to be possible theoretically in a one-step process with the polymeric sulfide-based oxidation method. This presupposes that the reactive sites on the polymer maintain their separation[15] during reaction. One end of the difunctional alcohol may then react with the chlorosulfonium ion **4** to form sulfoxonium intermediate **9**, thus leaving the other hydroxyl group unable to react with a second distant active site (Scheme II).

Scheme II



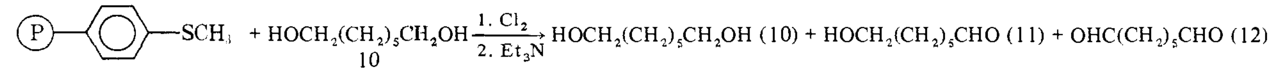
A method[16] of selectively blocking one functional group of a completely symmetrical difunctional alcohol via polymeric matrices is known. However, the application of this method to the present synthesis would require a three-step process.

Table II. Oxidation of 1-Octanol with *N*-Chlorosuccinimide[a]

Expt No.	Sulfide 3, mmol	Sulfur[b]	Octanol, mmol	Solvent[c]	Solvent, ml	Reaction temp, °C	Reaction time, hr	% aldehyde	% alkyl chloride	% unreacted alcohol
1	10.0	2.45	2.0	100	46	−40	6	58	42	0
2	2.5	2.45	0.5	50	46	−40	6	75.2	24.8	0
3	5.0	2.45	1.0	50	32	−40	4	75.3	24.7	0
4	2.5	2.45	0.5	30	56	−40	6	39.4	12.6	52
5	2.5	2.45	0.5	25	56	−40	6	20.8	4.2	75
6	2.5	2.45	0.5	15	66	−40	6	52.7	8.4	33.9
7	2.5	2.45	0.5	15	10	−40	6	0	0	100
8	5.7	1.13	1.0	0	50	−25 to −35	6	23.4	0	76.6

[a] Equal number of millimoles of *N*-chlorosuccinimide and sulfide 3 were used. [b] Millimoles of sulfur/gram of resin. [c] % CH$_2$Cl$_2$ in toluene.

Table III. Selective Oxidation of 1,7-Heptanediol[a]



Expt No.	Concn of sulfide moiety[b]	Sulfide used, total mmol	chlorine (as Cl_2), mmol	Reaction time, hr	Percent of product		
					Monoaldehyde **11**	Dialdehyde **12**	Diol **10**[d]
1	3.56	3.56	3.56	4	44.3	40.3	15.4
2	1.13	4.75	2.40	6	56.7	28.1	15.2
3	1.13	1.70	1.70	6	46.8	7.5	45.7
4	1.13	1.13	1.13	6	36.4	5.0	58.6
5	0.66	2.00	2.00	6	50.2	2.2	47.6
6	0.66	2.64	2.00	19	50.6[c]	5.0	0.5

[a] One millimole of diol was used in each reaction. [b] In millimoles of sulfur/gram of polymer. Attempts to prepare a polymer containing 0.1 mmol of S/gram of polymer were unsuccessful. [c] The remaining material (43.9%) was unidentified by-products. [d] Incomplete oxidation was primarily due to the insolubility of the diol.

The results from our study on the application of the polymeric sulfide-based oxidation of 1,7-heptanediol (**10**) are given in Table III. These results show that a significant degree of selectivity can be achieved using this technique. However, the formation of dialdehyde **12** from **10** indicates that some intrareaction occurs between reactive moieties attached to the resin.[17] The interaction between the functionalized sites may be caused either by the flexibility[17a] of the polymer chains or by the fact that the reacting sites (sulfide groups) are incorporated at random[15a] in the macro environment but not in the micro environment, therefore giving rise to "pockets" of high concentrations of reactive sites. From our method of synthesis of the polymeric sulfide, we have no assurance of randomness in the micro environment.

Although we chose macroreticular resins because of their rigidity, it is obvious that, at even moderate degrees of substitution (1.13 mmol/g), intraresin reactions are very prominent (see expt 2, Table III) when excess reagent is employed. The significant dilution effect from the low incorporation of sulfide groups (compare expt No. 1, 3, and 5 in Table III) in the polymer is definitely noticed and suggests the formation of dialdehyde is due to the polymer chain flexibility.

These experiments confirm in principle that a selective monooxidation of 1,7-heptanediol can be accomplished by these methods. However, at the present time, this does not appear to be competitive with classical methods from a practical standpoint. As is indicated by the last entry in Table III, attempts to consume all starting material by use of longer reaction times merely led to the formation of significant quantities of undesirable by-products. Undoubtedly future developments in the area of more rigid polymer matrices and unequivocal spacing of reactive groups in the *micro* environment would improve this technique. We are currently exploring further uses for these polymers.

Experimental Section

Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 137 spectrophotometer as KBr pellets. NMR spectra were recorded with a Varian T-60A instrument using tetramethylsilane as the internal standard ($\delta = 0$; $CDCl_3$ was the solvent). GLC analyses were carried out on a Varian Aerograph 920 Model instrument, equipped with a thermal conductivity detector. The columns used were commercially available (Varian) 4% FFAP (7 ft × 0.25 in.) on Chromosorb G (80-100 mesh). Short-path distillation refers to bulb-to-bulb distillation under reduced pressure using a Büchi Kugelrohr oven. Carbon tetrachloride and triethylamine were reagent grade, used as obtained and dried by other methods. Dichloromethane was dried by distilling from phosphorus pentachloride and stored over molecular sieves (3 Å). Toluene was reagent grade and dried over molecular sieves (3 Å).

Preparation of Poly(*p*-bromostyrene) (2).[10,12] Method A. To 13.0 g (125 mmol) of macroreticular polystyrene (Amberlite XE-305, Rohm & Haas) and 27.6 g (67.5 mmol) of thallic acetate sequihydrate ($Tl(OAc)_3 \cdot 1.5H_2O$) suspended in 200 ml of carbon tetrachloride was added dropwise with stirring 12.8 g (4.1 ml; 80 mmol) of bromine (as Br_2) in 30 ml of carbon tetrachloride, and the mixture was then stirred at 50-60° until all bromine color disappeared. The beads were filtered and washed with the following: (1) a mixture of 30% aqueous HCl and dioxane; (2) a mixture (1:1) of water and dioxane; (3) dioxane; (4) THF; (5) diethyl ether. The air-dried beads were further dried in vacuo (ca. 0.1 mmHg) at 50-60° overnight to yield 21.2 g of polymer. The brominated polystyrene **2** was refluxed in 500 ml of 0.1 *N* aqueous HCl solution, then in 50% aqueous dioxane, and finally in dioxane. Elemental analysis of vacuum-dried (ca. 0.1 mm) beads indicated that 3.56 mmol of bromine per gram of polymer had been incorporated (86% of added bromine).

Anal. Calcd for $(C_8H_7Br)_n$: Br, 43.70. Found: Br, 28.35.

Method B. To a suspension of 10.0 g (96 mmol) of macroreticular polystyrene (Amberlite XE-305, Rohm & Haas) and 0.1 g of anhydrous ferric chloride in 100 ml of carbon tetrachloride was added at room temperature a solution of 6 ml (112 mmol) of bromine (as Br_2) in 25 ml of carbon tetrachloride. The resulting mixture was stirred at ambient temperature for 24 hr and filtered. The beads were washed with acetone until no brown filtrate was obtained, then dioxane-H_2O (1:1) followed by dioxane. The brominated polymer was refluxed overnight in a Soxhlet apparatus equipped with a Dean-Stark water separator using a 2:1 mixture of benzene and dioxane, then dried in vacuo (ca. 0.1 mm) at 50° for 6 hr. Elemental analysis of the product indicated the incorporation of 3.61 mmol of bromine per gram of beads.

Anal. Calcd for $(C_8H_7Br)_n$: Br, 43.70. Found: Br, 28.83.

Preparation of Poly(*p*-methylmercaptostyrene) (3).[13] To a stirred suspension of 14.5 g (51.6 mmol of bromine) of dry poly(*p*-bromostyrene) **2** in 200 ml of tetrahydrofuran cooled to −78° under an argon atmosphere was added 50 ml of 2.28 *M* *n*-butyllithium-hexane (114 mmol) solution. The stirring was continued at −78° for 0.5 hr, then at room temperature for 1 hr, followed by removal of the tetrahydrofuran solution from the insoluble polymer by syringe. The beads were recharged at −78° with 150 ml of THF and 20 ml of 2.28 *M* *n*-butyllithium (68.4 mmol) and stirred at ambient temperature for 1 hr. The tetrahydrofuran was removed again, whereupon the polymer beads were treated with a mixture of 200 ml of THF and 20 ml of methyl disulfide (distilled) with stirring at −78° for 15 min and at room temperature for 0.5 hr and then refluxed under argon for 1 hr. The cooled mixture was diluted with 100 ml of water and filtered. The beads were washed with the following solvents: (1) water; (2) a 3:1 mixture of dioxane and water; (3) dioxane. Finally the air-dried beads were refluxed in a 2:1 mixture of benzene and dioxane in a Soxhlet apparatus equipped with a Dean-Stark water separator. After drying overnight under vacuum at 70°, there was obtained 11.4 g of beads. Elemental analysis indicated the incorporation[18] of 3.56 mmol of sulfur per gram of beads.

Anal. Calcd for $(C_9H_{10}S)_n$: S, 21.20. Found: S, 11.42.

Oxidation of Octanol. Method A. Chlorine as Coreactant. A solution of 280 mg (3.94 mmol) of chlorine (as Cl_2) in 10 ml of dichloromethane was added at −10° to a stirred suspension of 1.0 g (3.56 mmol of sulfur/gram of polymer) of poly(*p*-methylmercaptostyrene)[19,20] in 20 ml of dichloromethane, after which the mixture was cooled to −25°, treated with 130 mg (1.0 mmol) of octanol (distilled and stored over 3 Å molecular sieves) in 1.6 ml of dichloromethane and stirred at −25°. After 3 hr, 612 mg (6.0 mmol) of triethylamine in 2 ml of dichloromethane was added at −25°, and stirring was continued for an additional 20 min. The reaction mixture was diluted with 50 ml of ether, stirred for 10 min, and then filtered. The beads were collected by filtration and washed with another 30 ml of ether. The combined filtrates were next washed with 1 *N* hydrochloric acid solution and brine and dried ($MgSO_4$). After removal of the solvent, short-path distillation of the crude material at 50° (0.1 mm) afforded 243 mg (95.0%) of a colorless oil that contained 97.0% of octanal and 3.0% of octanol by GLC (4% SE-30; comparison with authentic samples).

Method B. *N*-Chlorosuccinimide as a Coreactant. To a stirred suspension of 2.06 g (5.0 mmol) of poly(*p*-methylmercaptostyrene)[19,20] (2.45 mmol of sulfur/gram of polymer) in 10 ml of a 1:1 mixture of dichloromethane and toluene was added slowly, at 0°, 670 mg (5.0 mmol) of *N*-chlorosuccinimide dissolved in 30 ml of a 1:1 mixture of dichloromethane and toluene. After stirring for 1 hr, 130 mg (1.0 mmol) of octanol in 2 ml of a 1:1 mixture of dichloromethane and toluene was added at −40°, and the mixture was stirred for an additional 4 hr. The mixture was treated with 600 mg (5.89 mmol) of triethylamine in 3 ml of a 1:1 mixture of dichloromethane and toluene, stirred at −40° for 15 min, then at room temperature for an additional 15 min, and filtered. The beads were washed with 70 ml of dichloromethane, and the combined filtrates were washed with 1 *N* hydrochloric acid and brine and dried ($MgSO_4$). After removal of the solvent, short-path distillation of the crude product at 60° (0.1 mm) yielded 100 mg (78%) of a colorless oil that contained 75.3% of octanal and 24.7% of octyl chloride by GLC (4% FFAP; comparison with authentic samples).

Oxidation of Prostaglandin Alcohol (6). To a stirred suspension of 2.0 g of poly(*p*-methylmercaptostyrene)[19,20] (2.66 mmol of sulfur/gram of polymer; 5.32 equiv) in 20 ml of dichloromethane was added, at −10°, 395 mg (5.0 mmol) of chlorine (as Cl_2) in 11 ml of dichloromethane, whereupon 352 mg (1.0 mmol) of prostaglandin intermediate alcohol **6** in 10 ml of dichloromethane was added and stirred at −40°. After 4 hr, 871 mg (8.6 mmol) of triethylamine in 2 ml of dichloromethane was added and the reaction mixture stirred at −40° for 5 min and then removed from the cooling bath. After 15 min, the mixture was filtered, and the beads were washed with three 25-ml portions of dichloromethane. The combined filtrates were washed with three 120-ml portions of ice-cold 1% (by volume) hydrochloric acid, water, and brine and dried ($MgSO_4$) while keeping the solution at 0°. The dried solution was concentrated to ca. 20 ml under a rotary vacuum at room temperature. The concentrate was chilled to 0°, then petroleum ether (20-40°) or *n*-hexane was added to precipitate out the product. After filtration, the mother liquid was further concentrated to precipitate out a second crop and the process repeated again. The first crop weighed 130.5 mg (white solid), the second crop 76.9 mg (white solid), and the third 168.0 mg (slightly gray solid). NMR comparison with that of an authentic sample[5b] indicated the product to be approximately 90% pure based on integration: NMR ($CDCl_3$) δ 5.08 (t, 1 H, J = 5 Hz, C—O—CH), 5.72 (m, 1 H, C—O—CH), and 9.80 (s, 1 H, -CHO). The product was homogeneous on silica gel TLC (1:1 ethyl acetate-hexane).

Oxidation of Benzyl Alcohol. A solution of 261 mg (3.3 mmol) of chlorine (as Cl_2) in 8 ml of dichloromethane was added slowly at −10° to a stirred suspension of 2.0 g of poly(*p*-methylmercaptostyrene)[19,20] (1.65 mmol of sulfur per gram of polymer; 3.3 equiv of sulfide group) in 38 ml of a 1:1 mixture of dichloromethane and *n*-hexane, after which the mixture was cooled to −25°, treated with 108 mg (1.0 mmol) of benzyl alcohol in 7 ml of dichloromethane, and stirred at −25° for 5 hr. A solution of 611 mg (6.0 mmol) of triethylamine in 5 ml of dichloromethane was added slowly and stirred at −25° for 20 min. The reaction mixture was filtered, and the beads were washed with three 25-ml portions of ether. The combined filtrates were washed with 1 *N* hydrochloric acid and brine and dried ($MgSO_4$). The conversion of benzyl alcohol to benzaldehyde (66.7%) and benzyl chloride (33.3%) was quantitative by GLC (5% SE-30). Reaction of the product mixture with 2,4-dinitrophenylhydrazine gave 150 mg (53%) of the 2,4-DNP derivative, mp 136-137° (lit. mp 137°).

Selective Oxidation of 1,7-Heptanediol (10).[22] To a stirred suspension of 3.04 g (2.0 mmol) of poly(*p*-methylmercaptostyrene),[19,20] containing 0.66 mmol of sulfur/gram of resin, in 20 ml of dichloromethane was added at −10°, a solution of 158 mg (2.0 mmol) of chlorine in 5 ml of dichloromethane, and the mixture was stirred at −10° for 5 min, after which 132 mg (1.0 mmol) of 1,7-heptanediol[21] in 10 ml of dichloromethane was added at −25°. After stirring for 6 hr, 655 mg (6.42 mmol) of triethylamine in 5 ml of dichloromethane was added in one portion and the mixture stirred at −25° for 5 min, then warmed to room temperature for another 10 min. The mixture was filtered, and the beads were washed with three portions of 15 ml of ethyl acetate. The combined organic solution was concentrated[18] to ca. 2 ml and refiltered. The crude product was analyzed directly by GLC (4% FFAP on Chromosorb G, 7 ft × 0.25 in., 200°) and found to contain 7-hydroxyheptanal (**11**) (50.2%), 1,7-heptanedial (**12**) (22%), and 1,7-heptanediol (**10**) (47.6%). The mono- and dialdehydes were isolated and confirmed by ir and NMR.

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(18) The sequence employed for introducing the methyl sulfide moiety onto polystyrene was highly reproducible, and the percentage of sulfur incorporated could be easily adjusted as desired.
(19) The product yields were not effected by the sulfur concentration of the polymer[18] above approximately 2 mmol/g, whereas reaction rates were proportional to sulfur content. However, product yields *were* dependent on the number of milliequivalents of sulfide employed. In general, a minimum of 3–3.5 mequiv of sulfur/mequiv of alcohol was required for maximum yields. In some cases, higher equivalents were used in order to increase reaction rates and prevent side reactions.
(20) Recycled polymer should be dried by azeotroping with a 2:1 mixture of benzene and dioxane in a Soxhlet apparatus equipped with a Dean-Stark water separator.
(21) 1,7-Heptanediol (95% pure) was dried by the following procedure. The alcohol was dissolved in dichloromethane, and benzene was added until the solution lost its clearness. The solvent was removed on a rotary evaporator, and this process was repeated two or three times.