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Synthesis of Polyurethane Graft Copolymers by Polyaddition Reaction of Dihydroxyl-Terminated Macromonomers

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Summary

Polyurethane-poly(methyl methacrylate) graft copolymers of well-defined structure and composition were synthesized by macromonomer method. Dihydroxyl-terminated macromonomer was prepared by radical polymerization of methyl methacrylate in the presence of α-thioglycerol as a chain transfer agent. This dihydroxyl-terminated macromonomer and 1,4-butanediol were added to diisocyanate (hexamethylene diisocyanate or toluene-2,4-diisocyanate) catalyzed by di-n-butyltin dilaurate to produce tailor-made graft copolymers.

Introduction

Considerable interest has been shown in the syntheses of tailor-made graft copolymers for the design of the functional materials. Among various methods of preparation of graft copolymers, use of macromonomers may be one of the most promising approaches. Thus, a number of vinyl-type macromonomers have so far been prepared (for example, ITO et al. 1980, YAMASHITA 1981a, MASSON et al. 1982, VARGAS et al. 1982). Recently we have extended the concept of macromonomers to those with dicarboxyl-end groups, so-called condensation-type macromonomers (YAMASHITA et al. 1981b). Use of this macromonomer may be serviceable to modify the condensation-type polymers such as polyamides. Here, as a series of these studies, we report the synthesis and the reaction of polyaddition-type macromonomers, which have dihydroxyl-end groups.

Results and Discussion

The synthesis of dihydroxyl-terminated macromonomer (2) was carried out by radical polymerization of methyl methacrylate in the presence of α-thioglycerol (1) as a chain transfer agent (Scheme I). A mixed solvent system of tetrahydrofuran and ethanol (10:7) should be used to get a homogeneous solution. The purification of 2 was performed by reprecipitation from benzene into petroleum ether and from acetone into water. The results of the preparation of 2 are summarized in TABLE 1. The molecular weight of 2 was calculated on the basis of GPC by using calibration curve for polystyrene, which was also determined from the hydroxyl group content

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determined by titration. The hydroxyl group content was measured by the reaction with acetic anhydride in pyridine followed by hydrolysis and titrating the residual acetic acid in tetrahydrofuran with 0.02 N aqueous potassium hydroxide. As shown in TABLE 1, the molecular weight determined by titration is generally smaller, i.e. high hydroxyl group content, and this may be due to the errors arising out of the very sensitive nature of the titration process to moisture. However, using a nitrogen atmosphere for titration did not give better results. 2 of a desired molecular weight (3000 - 5000) can be readily prepared by controlling the feed ratio of the monomer to 1 in the low conversion. As shown in Figure 1a, the IR spectrum of 2 shows characteristic stretching bands at 3500 cm^{-1} (νO-H), 1720 cm^{-1} (νC=O) and 1140 cm^{-1} (νC-O). The solubility of 2 in organic solvents is similar to that of the ordinary poly(methyl methacrylate).

The macromonomer (2) and 1,4-butanediol (3) were added to 1,6-hexamethylene diisocyanate (4a) catalyzed by di-n-butyltin dilaurate in N-methyl-2-pyrrolidone at 80°C (Scheme I). To get a relatively high molecular weight graft copolymer, the combined amount of 2 and 3 should be equal to the amount of 4a. The graft copolymer (5a) was isolated by reprecipitation from m-cresol into a mixed solvent of acetone and methanol, which dissolved unreacted 2. The structure of 5a was confirmed by IR, ^{1}H-NMR and elemental analysis (see experimental section). IR spectrum of 5a (Figure 1b) shows the absorptions at 3300 cm^{-1} (νNH), 1530 cm^{-1} (δNH) and 1240 cm^{-1} (νC-N). The carbonyl absorptions near 1700 cm^{-1} appear broad peak due to the overlap of two carbonyl stretching bands of urethane and carbomethoxy groups. From the ^{1}H-NMR spectrum of 5a (Figure

TABLE 1

Synthesis of Dihydroxyl-Terminated Macromonomer[a)]

Run	$[I]_0/[M]_0$ ($\times 10^{-3}$)	$[S]_0/[M]_0$ ($\times 10^{-2}$)	Time (h)	Yield (%)	$\bar{M}n$ ($\times 10^3$) GPC[b)]	$\bar{M}n$ ($\times 10^3$) Tit[c)]	$\bar{M}w/\bar{M}n$	Cs[d)]
1	10.4	2.09	2.0	24.5	5.8	5.4	1.61	0.889
2	10.4	4.48	2.5	32.5	4.3	3.4	1.51	0.632
3	10.5	4.50	1.5	35.5	3.7	3.2	1.49	0.670
4	6.4	4.62	1.0	14.2	3.5	3.1	1.54	0.706

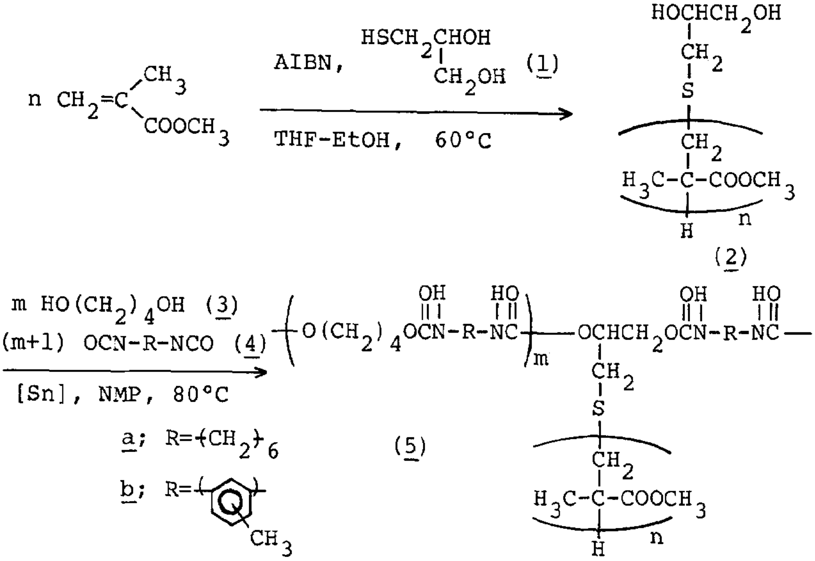
a) Reactions were carried out at 60°C in THF-EtOH. [I]=[AIBN], [S]=[α-thioglycerol], [M]=[MMA]

b) Calculated by using calibration curve for polystyrene.

c) Determined by end-group titration assuming two hydroxyl groups per molecule.

d) Calculated from $Cs=\log(1-\alpha[M]_0/n[S]_0)/\log(1-\alpha)$
α;conversion, n;degree of polymerization

Scheme I



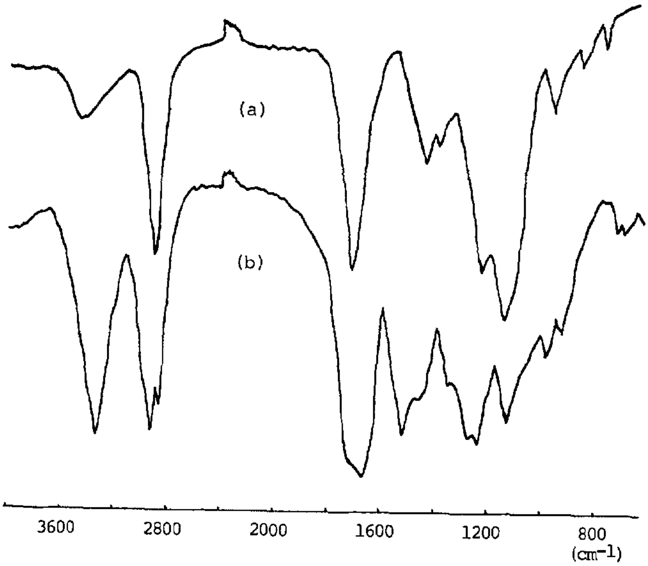


Figure 1. IR spectra of PMMA-macromonomer(a)(2) and graft copolymer(b)(5a) (KBr)

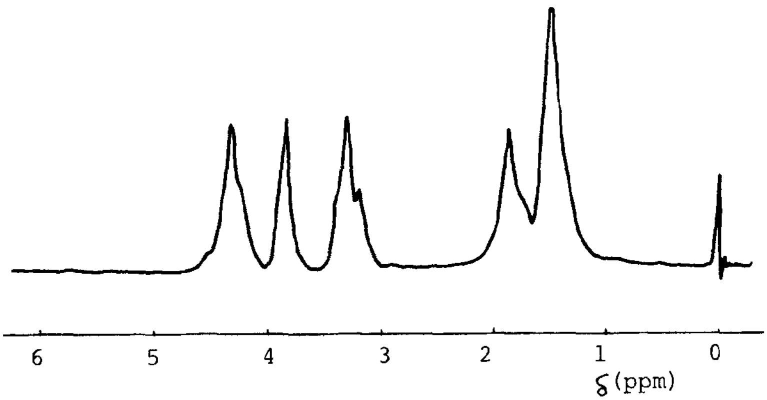


Figure 2. ^{1}H-NMR spectrum of graft copolymer (5a) (in CF_3COOH)

2), MMA content in the copolymer can be calculated. These results are summarized in TABLE 2. Compared with wt% of MMA in the feed, the decrease of MMA content in the graft copolymer was obserbed. This result may be explained by assuming that the reprecipitation and the washing removed the low molecular weight fraction of polyurethane, which possessed a higher content of PMMA.

Instead of 4a, toluene-2,4-diisocyanate (4b) can be used and the corresponding graft copolymer (5b) was produced (Scheme I). The result of the formation of 5b is shown in TABLE 2 (Run 5).

Experimental section

Materials

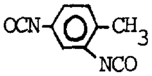
Commercial methyl methacrylate (MMA) was distilled under vacuum prior to use. α,α'-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. α-Thioglycerol, 1,4-butanediol, 1,6-hexamethylene diisocyanate, toluene-2,4-diisocyanate and di-n-butyltin dilaurate were commercially available and used without further purification. N-Methyl-2-pyrrolidone (NMP) was dried over molecular sieves and distilled under nitrogen. Tetrahydrofuran (THF), ethanol, pyridine, m-cresol and acetic anhydride were distilled under nitrogen atmosphere.

Macromonomer (2)

A typical example is as follows. MMA, α-thioglycerol, AIBN, THF and ethanol were placed in a glass ample and sealed under vacuum. Polymerization was carried out at 60°C for 1.0 - 2.5 hours. The macromonomer was precipitated into petroleum ether, purified twice by reprecipitation from benzene into petroleum ether, once from acetone into water, then freeze-drying under vacuum. The hydroxyl group content was determined by the following procedure. The macromonomer

TABLE 2

Synthesis and Characterization of Graft Copolymers$^{a)}$

		Feed			Polymer			
Run	Diisocyanate	2 (Mn)$^{b)}$	2 (mol%)$^{c)}$	MMA (wt%)	Yield (%)	PMMA$^{d)}$ (mol%)$^{c)}$	MMA$^{d)}$ (wt%)	$\eta_{sp/c}$$^{e)}$
1	$OCN(CH_2)_6NCO$	5400	2.03	24.1	87.3	1.17	19.5	1.08
2	〃	3200	4.46	36.2	60.5	2.48	23.2	0.18
3	〃	3100	9.31	55.6	39.7	5.05	37.4	0.18
4	〃	3100	14.77	65.4	45.2	8.13	48.5	0.27
5		3100	6.43	43.4	54.3	3.84	31.4	0.30

a) Reactions were carried out at 80°C in NMP (N-methyl-2-pyrrolidone) in the presence of $(n\text{-}Bu)_2Sn[OOC(CH_2)_{10}CH_3]_2$ ([Sn]/[4]=5x10^{-4}).
b) Calculated by end-group titration.
c) mol% of 2; [2]/([2]+[3])x100
d) Calculated from ^{1}H-NMR.
e) Measured in m-cresol at 30°C. c=0.5 g/dl

was reacted with the acetylating agent (a mixture of acetic anhydride and pyridine, 1:7) under nitrogen at 90 - 100°C for 2 hours. After the heating, addition of THF and water hydrolyzed the excess acetic anhydride. This solution was titrated by 0.05N KOH aqueous alcohol under nitrogen using 0.1% cresol red and 0.1% thymol blue as an indicator. The hydroxyl group content was calculated by the difference between the above value and that of the blank test.

Graft Copolymer (5)

A typical procedure is as follows. Under nitrogen, a mixture of 2, 3, 4a, di-n-butyltin dilaurate and NMP was placed in a flask equipped with a reflux condenser and heated at 80°C for 6 hours. The resulting reaction mixture was poured into methanol. The polymer was obtained almost quantitatively and purified by reprecipitation from m-cresol into water-methanol and drying in vacuo. The elemental analysis of 5a (Run 1 in TABLE 2) is C 56.42%, H 8.77%, N 8.35 %. This result is in fair agreement with that calculated from the ^{1}H-NMR spectrum (C 56.56%, H 8.41%, N 8.71%).

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