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Synthesis of telechelic vinyl polymers by a two-component iniferter

Iwhan Cho*, Jinseuk Kim

Department of Advanced Materials Engineering, Korea Advanced Institute of Science and Technology, PO Box 201, Cheongryang 135-650, Seoul, South Korea

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Abstract

α,ω-Hydroxy-terminated vinyl prepolymers were prepared by radical polymerization of methyl methacrylate, butyl acrylate, styrene and vinyl acetate in the presence of allyl alcohol. The butyl acrylate prepolymer of molecular weight 3100 and functionality 2.2 was prepared by the following condition; [BA] = 3.85 mol/l, [ACPROL] = 0.128 mol/l and [AA] = 0.90 mol/l at 110°C. The polyurethane reactions of the resulting telechelic polymers with hexamethylene diisocyanate were carried out to obtain vinyl polymer-based polyurethanes.

Keywords: Vinyl prepolymer; Radical polymerization; Allyl alcohol

1. Introduction

In traditional practice, α,ω-hydroxy-terminated vinyl polymers are prepared by the anionic polymerization process [1,2]. In the "Group-Transfer Polymerization (GTP)", functionalized initiators can be used to prepare telechelic prepolymer of acrylate monomers [3,4]. However, the rigorous polymerization conditions such as low polymerization temperature, highly purified solvents and monomers, etc., are not practical for commercial operations. As alternatives, several radical techniques based on functional azoinitiators and free radical redox systems have also been introduced [5,6].

In 1982, Otsu proposed the concept of an iniferter for the control of terminal functions of polymers [7,8]. An iniferter is designed as an initiator which also functions as a chain transfer agent and as a primary radical terminator. Several workers have reported on the characteristics and mechanism of polymerizations and end group control with the use of iniferters [9–11]. In the synthesis of α,ω-bifunctional polymers by radical polymerization, it is necessary to use appropriate solvents or compounds with large chain transfer constants along with the radical initiator.

In the present work, we have studied a new *ini*tiator–trans*fer* agent–*ter*minator (iniferter) system consisting of two compounds with the same functional group, one as an initiator and the other as a chain transfer agent. When radical polymerization is carried out in the presence of these compounds, the resulting polymers also have the same functional group at both chain ends. We prepared vinyl polymers bearing hydroxyl group at both chain ends from various vinyl monomers with a two-component iniferter system, 4,4′-azobiscyanopropanol(ACPROL) and allyl alcohol(AA) as initiator and chain transfer agent, respectively.

2. Experimental

2.1. Materials

All the monomers, methyl methacrylate (MMA), styrene (St), vinyl acetate (VAc), butyl acrylate (BA), allyl alcohol (AA) were treated with an inhibitor removal column, DHR-4 (Scientific Polymer Production Company) before use, then stirred with calcium hydride for one day and distilled. Hexamethylene diisocyanate (HMDI) and dibutyl tin dilaurate (DBTDL) were used as received from the reagent company. Acetyl propanol was fractionally distilled under reduced pressure, and the middle fraction was used. ACPROL was prepared from acetyl propanol and hydrazine dichloride according to the known method [5]. The solid product was recrystallized from chloroform–hexane (yield 66.4%).

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* Corresponding author.

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2.2. Polymerization procedures

Polymerization was carried out in sealed glass tubes after degassing by three alternate freeze–pump–thaw cycles. The polymerization tube was placed in a thermostated oil-bath for a certain time period. After polymerization reaction, the reaction mixtures were poured into a large volume of nonsolvent to isolate the polymer. The polymers were purified by repeated reprecipitations.

2.3. Measurements

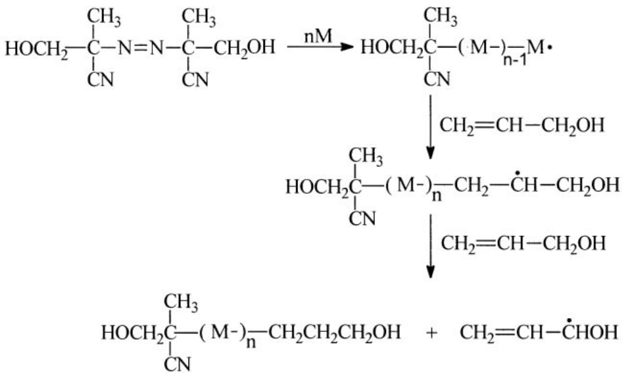
The number- and weight-average molecular weights ($\overline{Mn}$ and $\overline{Mw}$) were determined by gel permeation chromatography(GPC) at 40°C with tetrahydrofuran(THF) as eluent, as calibrated with polystyrene standards. The hydroxyl end group of the produced vinyl prepolymer was measured by Polyol Analyzer (Near-Infrared Spectroscopy, NIR System, Inc.). The calibration of hydroxyl groups was done using ACPROL initiator.

3. Results and discussion

3.1. Preparation of hydroxy-terminated polystyrene

A series of reactions were conducted with St using different amounts of chain transfer agent (AA). The polymerization reaction of the present system can be represented as in Scheme 1.

Staudinger believed that no polymer could be obtained from AA [12]. The ready abstraction of an allylic hydrogen by the chain end radical of the growing polymer leads to the formation of a stable allyl radical which is virtually incapable of reinitiation. The transfer reaction thus leads to termination of the polymerization. However, there are reports that St and AN were copolymerized with AA and relatively high molecular weights of copolymer were obtained [13–16]. Also, they confirmed that the addition of AA to the radical polymerization of vinyl monomers can be used to give polymers of controlled low molecular weight and to obtain polyfunctional polymers. Scheme 1 is probably an oversimplification but can give the correct answer nevertheless.



Scheme 1.

When AA was added to polymerization systems, the conversion was decreased at high concentration of AA and $\overline{Mn}$ of poly(St) also decreased. From the plotting of the reciprocal of the polymerization degree ($\overline{P}$D against [AA], the chain transfer constant of poly(St) radical toward AA was found to be 2.16×10^{-2}. This value is 100 times larger than chain transfer constant toward St monomer ($C_m = 0.07 \times 10^{-4}$), poly(St) ($C_p = 0.8 \times 10^{-4}$), and it is also larger than the reported value of disulfide (C_s; toward disulfide is 1.85×10^{-2}) [10], indicating that AA was an effective chain transfer agent in this polymerization system.

The functionalities of the polymer were calculated using the expression

$$\text{Functionalities}(\overline{N}) = \overline{Mn}/\text{equivalent weight}$$

where the equivalent was obtained from hydroxyl analysis. The values of $\overline{N}$ were always nearly two (Table 1). Because the termination mode of styrene polymerization is mainly combination, the functionalities were nearly two irrsespective of [AA]. From these results, the two-component iniferter system, ACPROL and AA, was confirmed to be effective for synthesis of the α,ω-dihydroxy poly(St).

3.2. Preparation of hydroxy-terminated polyvinyl acetate

The propagating radical of vinyl acetate is highly reactive and the chain transfer toward AA should occur easily, and the chain end structure of the resulting polymer can be controlled more effectively than styrene.

Values in Table 1 show that number-average molecular weight decreases as [AA] increases. The functionalities of poly(VAc) were always larger than two. The conversion of VAc was abruptly decreased at high concentrations of AA. These observations indicate that AA was acting as an effective transfer agent in the polymerization of VAc.

Table 1
Radical polymerization of St and VAc monomer with ACPROL and AA in THF at 100°C for 3 h

Monomer	[AA] (%)	Conversion (%)	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	$\overline{N}$
St[a]	0	82.8	5320	1.66	1.96
	0.19	84.3	5286	1.60	1.96
	0.95	83.0	4330	1.70	2.01
	1.90	68.3	3580	1.75	2.03
	0.95[d]	83.5	4700	1.77	0.85
VAc[b]	0	98.2	2950	2.41	2.46
	0.045	95.3	2790	1.95	2.32
	0.225	81.9	2400	1.94	2.21
	0.450	52.9	1900	2.09	2.28
	0.225[c]	85.6	2530	1.77	2.05

[a] [St] = 3.85 mol/l; [ACPROL] = 0.19 mol/l

[b] [VAc] = 3.85 mol/l; [ACPROL] = 0.045 mol/l.

[c] Initiated with AIBN instead with ACPROL.

Table 2
Radical polymerization of MMA and BA monomer with ACPROL and AA in THF at 100°C for 3 h

Monomer	[AA] (%)	Conversion (%)	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	$\overline{N}$
MMA[a]	0	90.1	7110	2.37	0.71
	0.154	88.2	6620	2.17	1.22
	0.770	84.5	5680	1.95	1.95
	1.540	73.6	4920	2.02	2.03
	0.770[d]	83.1	6120	1.65	0.62
BA[b]	0	93.8	7120	1.98	0.86
	0.096	92.4	6450	1.75	1.81
	0.480	90.9	5460	1.91	2.15
	0.960	70.3	4230	1.88	2.19
	0[c]	96.5	2620	2.23	0.96
	1.92[c]	68.7	1650	2.18	2.35
	0.48[d]	91.5	5940	1.85	0.77

[a] [MMA] = 3.85 mol/l; [ACPROL] = 0.154 mol/l.
[b] [BA] = 3.85 mol/l; [ACPROL] = 0.096 mol/l.
[c] [BA] = 3.85 mol/.; [ACPROL] = 0.384 mol/l.
[d] Initiated with AIBN instead with ACPROL.

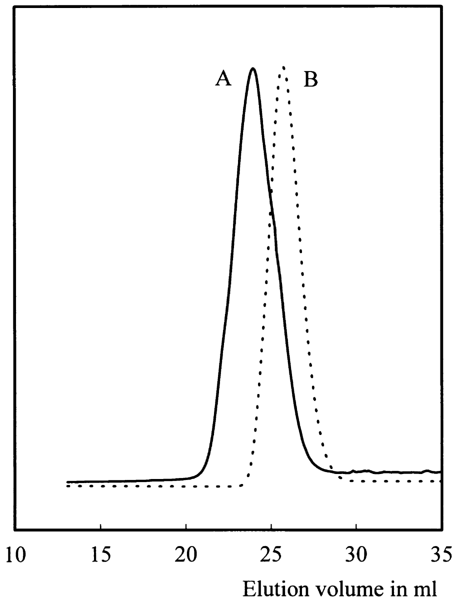


Fig. 1. Typical GPC elution curves; A) the resulting polyurethane polymer with HMDI at 60°C for 10 hr, B) the parent poly(St).

3.3. Preparation of hydroxy-terminated acrylate polymer

Table 2 shows the results of polymerization of MMA and BA with ACPROL and AA. In the polymerization of MMA, $\overline{Mn}$ decreased slightly with increasing [AA]. The functionalities were nearly two at high concentrations of [AA]. In the polymerization of BA, $\overline{Mn}$ decreased with increasing [AA] to a greater degree than MMA polymerization. We also investigated the molecular weight variation with initiator concentration for the possible preparation of low viscosity polyol. The functionalities of BA were always larger than two with excess of AA, and BA prepolymer can be used for subsequent polycondensation. This result suggests that this two-component iniferter system, ACPROL and AA, may be used to synthesize telechelic acrylate prepolymers.

3.4. Synthesis of polyurethane polymer

Finally, we attempted to synthesize a polyurethane polymer by use of the HMDI and the telechelic vinyl prepolymer, PS, PVAc, PMMA, and PBA, prepared by two-component iniferters.

The hydroxyl peak of the parent polymer disappeared and the amide peak at 1734 cm^{-1} appeared with polyurethane reaction. Table 3 shows the characteristics of the starting polymers and the resulting polymers. Fig. 1 shows the GPC elution curves for the parent poly(St) and the resulting polyurethane polymer, respectively. From the GPC chromatogram, the number average molecular weight of the starting poly(St) was increased from 3480 to 22 000 (Table 3). The glass transition temperatures of the resulting polyurethane polymers were also higher than the parent prepolymer (Table 3). Therefore, we successfully synthesized the polyurethane polymer based on the telechelic vinyl polymer prepared by the new two-component iniferter system.

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Table 3
The results of polyurethane reaction by telechelic vinyl prepolymer with HMDI in THF at 60°C for 10 h[a]

	Parent polymer				Resulting polymer		
Vinyl monomer	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	$\overline{N}$	T_g (°C)	$\overline{Mn}$	$\overline{Mw}/\overline{Mn}$	T_g (°C)
St	3480	1.68	20.1	66.7	22 000	2.59	94.7
VAc	2220	2.01	2.25	2.8	11 500	2.89	18.2
MMA	3970	2.25	2.02	77.7	28 100	1.77	98.5
BA	3100	2.12	2.20	−45.8	18 860	2.39	−33.1

[a] The polyurethane reaction was catalyzed by dibutyl tin dilaurate.The functionalities were determined by the traditional titration method.

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