Macromolecules 1990, *23*, 935-939

Synthesis of Sequence-Ordered Copolymer. Synthesis of Ethylene–Methyl Methacrylate Alternating Copolymer by a Polymer Reaction

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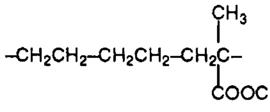
Received April 17, 1989; Revised Manuscript Received July 3, 1989

ABSTRACT: Ethylene–methyl methacrylate alternating copolymer, which could not be obtained directly from ethylene and methyl methacrylate monomers, was synthesized by reducing vinyl bromide–methyl methacrylate alternating copolymer. Among several reduction experiments studied, radical-initiated reduction with tri-*n*-butyltin hydride at −20 °C was successful and yielded ethylene–methyl methacrylate alternating copolymer with only 2% lactone units formed by a side reaction. The ethylene–methyl methacrylate alternating copolymer was atactic and amorphous. It was soluble in several organic solvents and was a soft and rubbery material.

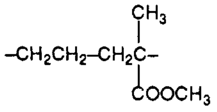
We reported earlier[1] the synthesis of an ethylene–ethylene–methyl methacrylate periodic copolymer by hydrogenating a butadiene–methyl methacrylate alternating copolymer. This periodic copolymer was a soluble, partially crystalline, soft and tough material. Crystalline structure should come from its ordered sequence. Several other two ethylene–one acrylate periodic copolymers were also reported.[1,2] Some were crystalline and others were not.

Our next interest is to compare this periodic copolymer (1) with ethylene–methyl methacrylate alternating copolymer (2); the latter has one ethylene unit less than the periodic copolymer 1.



$$-CH_2CH_2-CH_2CH_2-CH_2\overset{CH_3}{\underset{COOCH_3}{C}}-$$

1

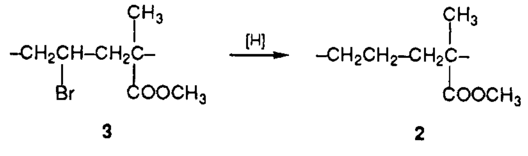


$$-CH_2CH_2-CH_2\overset{CH_3}{\underset{COOCH_3}{C}}-$$

2

Attempted alternating copolymerization of ethylene and methyl methacrylate in the presence of Lewis acid, however, was unsuccessful under several experimental conditions. Even with a large excess of ethylene feed, which led to a successful synthesis of ethylene–methyl acrylate alternating copolymer,[3,4] 2 was not obtained, apparently because of α-methyl substitution in the acrylate unit and poor donor character of ethylene.[5]

The present paper describes the synthesis of 2 by reducing a vinyl bromide–methyl methacrylate alternating copolymer (3).



$$\underset{\mathbf{3}}{-CH_2\underset{Br}{C}H-CH_2\overset{CH_3}{\underset{COOCH_3}{C}}-} \xrightarrow{[H]} \underset{\mathbf{2}}{-CH_2CH_2-CH_2\overset{CH_3}{\underset{COOCH_3}{C}}-} \quad (1)$$

Experimental Section

Materials. Commercial extra-pure vinyl bromide and methyl methacrylate were used. Gaseous vinyl bromide was condensed and measured before use. Methyl methacrylate was washed with saturated sodium hydrogen sulfite, 5% sodium hydroxide, and saturated sodium chloride and dried over anhydrous sodium sulfate. Distilled monomer was stored over calcium hydride in a refrigerator and again distilled before use. Toluene for copolymerization and tetrahydrofuran (THF) for reduction experiments were extra-pure reagents, purified as usual and dried over sodium. Ethylaluminum sesquichloride (EASC) from the Ethyl Corp. was distilled under vacuum and dissolved in toluene (4 mol/L). Reducing reagents, sodium cyanoborohydride, sodium hydride, 55% hydroiodic acid, and tri-*n*-butyltin hydride were commercial extra-pure reagents and used as received. Recrystallized benzoyl peroxide (BPO) and α,α′-azobis(isobutyronitrile) (AIBN) were radical initiators.

Copolymerization. In a nitrogen-purged and cooled 100-mL pressure-reaction vessel, methyl methacrylate was taken and degassed. The volume of EASC solution was calculated, and, if necessary, a radical initiator or a solvent toluene was added also at dry-ice temperature. Finally, vinyl bromide was condensed at −20 °C into the reaction vessel. All procedures were carried out under nitrogen. The vessel was placed in a temperature-controlled bath for a given time with occasional shaking. After copolymerization, the vessel was again cooled at dry-ice temperature, and excess methanol containing 1% hydrochloric acid and a trace of hydroquinone was slowly added. The supernatant solution with copolymer precipitate was left standing overnight in a hood to remove unreacted vinyl bromide. The collected copolymer was reprecipitated three times from chloroform solution into methanol and dried under vacuum. Copolymerization of vinyl chloride and methyl methacrylate was also studied with similar procedures.

Reduction. Four reduction experiments were carried out. A copolymer sample prepared under the conditions of run 9 of Table I (see below) was subjected to the most experiments.

(1) A dimethyl sulfoxide (20 mL) solution of copolymer (0.60 g) and sodium cyanoborohydride (0.5 g) was stirred at room temperature. After 50 h, the product copolymer was precipitated into methanol, reprecipitated from chloroform solution into methanol, dried in vacuo, and weighed 0.40 g.

(2) Into a stirred solution of copolymer (0.22 g) in THF (5 mL)–sulfolane (5 mL) was added portionwise sodium hydride (0.43 g). After 170 h, workup was the same as in experiment (1). The product copolymer weighed 0.10 g.

(3) A mixture of copolymer (1.0 g), red phosphorus (0.5 g), and 55% hydroiodic acid (5 mL) was refluxed for 130 h at 130 °C. The product copolymer was precipitated into methanol, reprecipitated from hot acetic acid solution into methanol, dried in vacuo, and weighed 0.61 g.

(4) A solution of copolymer (1.0 g), tri-*n*-butyltin hydride, and AIBN in THF was prepared in a reaction vessel at dry-ice temperature. The vessel was maintained at a reaction temperature with or without tungsten lamp irradiation. Detailed reaction conditions will be given in the Results and Discussion. After a given time, a small volume of methanol was slowly added to the reaction mixture at dry-ice temperature to decompose tin compounds. Further workup was the same as in experiment (1), and the product copolymer weighed 0.58 g in run 7 of Table III.

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Table I
Copolymerization of Vinyl Chloride or Vinyl Bromide and Methyl Methacrylate

run	monomer feed,[a] mol %		Lewis acid[b]	initiator[c]	temp, °C	time, h	yield,[d] %	copolymer compositn,[a] mol %	
	VC	VB						VC	VB
1	80		EASC		-20	28	1.3	0	
2	80		BCl_3		-20	50	4.1	0	
3	80		BCl_3	BPO	-20	50	0.7	0	
4	80		EASC	BPO	-20	24	58.2	41.6	
5	90		EASC	BPO	-20	21	26.3	45.3	
6	95		EASC	BPO	-20	20	15.8	46.9	
7		80	EASC		0	50	7.5		35.6
8		80	EASC	BPO	0	4	36.9		40.6
9		90	EASC	BPO	0	2	51.4		50.2

[a] VC, vinyl chloride in runs 1–6; VB, vinyl bromide in runs 7–9. [b] Equimolar to methyl methacrylate and BPO was added. [c] 2 mol % based on methyl methacrylate was added. [d] Yield based on methyl methacrylate.

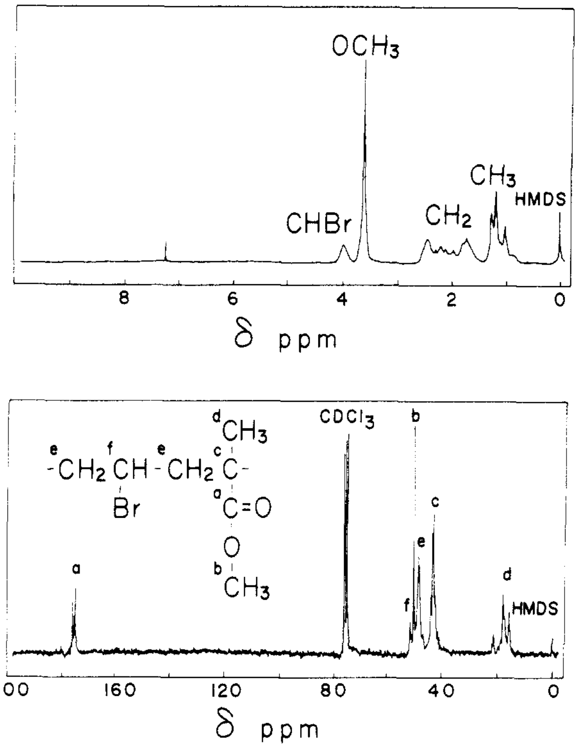


Figure 1. 200-MHz ^1H and 50-MHz ^{13}C NMR spectra of vinyl bromide–methyl methacrylate alternating copolymer in $CDCl_3$.

Measurement. ^1H (200-MHz) and ^{13}C (50-MHz) nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-200 spectrometer. The pulse sequence for ^{13}C NMR was as follows: 18-μs pulse width (90° pulse angle), 0.8-s acquisition time, and 1-s interval. Generally, 800 scans were accumulated for a 12 500-Hz spectral width. ^1H (60-MHz) NMR spectra were also recorded on a Hitachi R-24A spectrometer. Most determinations were carried out for 5–10% deuterochloroform solutions at room temperature. Infrared (IR) spectra were recorded on a Jasco IR-E spectrometer for film samples. Differential scanning calorimetry (DSC) study was carried out on a Rigaku-Denki Thermoflex with a low-temperature unit. Molecular weight was estimated by using a Tosoh gel permeation chromatograph HLC 803D with reference to polystyrene standards. The solvent was THF, and its flow rate was 1 mL min^{-1}.

Results and Discussion

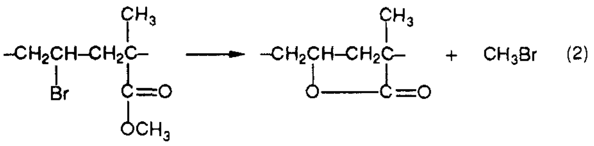
Alternating Copolymerization. Table I, runs 1–6, shows copolymerization of vinyl chloride and methyl methacrylate in the presence of EASC or boron trichloride with or without BPO at -20 °C. Even with the largest excess of vinyl chloride (run 6), the vinyl chloride content in the product copolymer was 46.9%, which was a somewhat, but certainly less, value than the value (50%) requisite for an alternating copolymer. A lactonization experiment (as in eq 2 for a vinyl bromide copolymer) in which this run 6 copolymer sample was heated at 100 °C showed a constant 70.4% lactone unit content after 3 days. Theoretically (see below), a perfectly alternating copolymer should show 86.5% lactone unit. Both results, on the copolymer composition and lactonization, show the copolymer is not pure enough as to the alternating structure for the reduction reaction (eq 1).

Table II
^1H NMR Absorptions[a] of Vinyl Bromide and Methyl Methacrylate Homopolymers and Their Alternating Copolymer

	$-CH_3$	$-CH_2-$	$-CHBr-$	$-COOCH_3$
poly(vinyl bromide)		1.8–3.0	4.1–5.0	
alternating copolymer	0.9–1.5	1.5–2.6	3.8–4.2	3.8
poly(methyl methacrylate)	0.6–1.5	1.5–2.4		3.7

[a] In ppm from hexamethyldisiloxane (HMDS) in $CDCl_3$ solutions.

The results of copolymerization with a stronger donor monomer, vinyl bromide, are shown in Table I, runs 7–9. Under the conditions of run 9 with a 90 mol % of vinyl bromide feed, a copolymer containing almost 50 mol % vinyl bromide units was obtained in good yield. Its ^1H and ^{13}C NMR spectra are shown in Figure 1, and the ^1H NMR absorptions are compared with those of both homopolymers in Table II. Each of the ^1H absorptions of the copolymer more or less shifted from that of homopolymers. Especially, the copolymer's absorptions due to $COOCH_3$ and CHBr groups were readily distinguishable from the homopolymers' absorptions. In the copolymer's spectrum, any appreciable absorption was not observed at where these two groups in homopolymers gave absorptions. This is evidence for the alternating structure of the copolymer. Further evidence is given by a lactonization experiment. When a solid sample of the copolymer was heated at 70 °C, a reaction between neighboring C–Br and $-COOCH_3$ groups (eq 2) occurred



$$-CH_2\underset{Br}{CH}-CH_2\overset{CH_3}{\underset{\underset{OCH_3}{C=O}}{C}}- \longrightarrow -CH_2\underset{O}{CH}-CH_2\overset{CH_3}{\underset{C=O}{C}}- \quad + \quad CH_3Br \qquad (2)$$

and a lactone unit was formed. The extent of lactonization can be predicted according to Flory's theory.[6,7] A perfectly alternating copolymer should lead to 86.5% lactone formation in the heated copolymer. After 20 h at 70 °C, the heated copolymer showed new C=O absorption at 1760 cm^{-1} in its IR spectrum, as well as new CHOCO and weakened $COOCH_3$ and CHBr absorptions in its ^1H NMR spectrum (Figure 2). Both indicate lac-

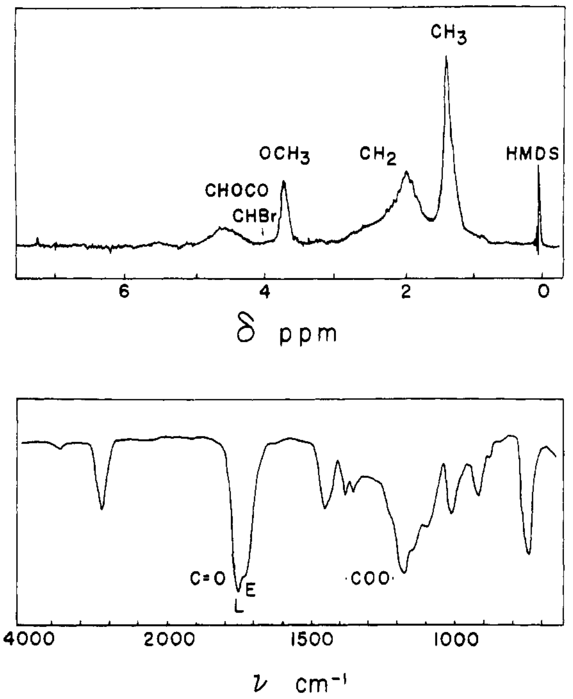
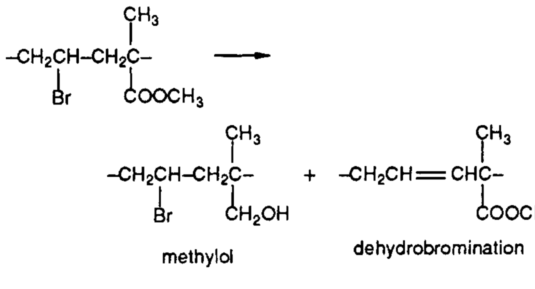


Figure 2. 60-MHz ^1H NMR and IR spectra of heated and lactonized vinyl bromide–methyl methacrylate alternating copolymer. E and L in the IR spectrum indicate ester and lactone C=O stretching absorptions, respectively.

tone formation, and the lactone unit content estimated from the ^1H NMR spectrum was 85.7% in agreement with the prediction. This is further evidence for the highly alternating structure of the Run 9 copolymer before heating.

Reduction. Four reagents were studied for the reduction of vinyl bromide–methyl methacrylate alternating copolymer: (1) sodium cyanoborohydride, (2) sodium hydride, (3) hydroiodic acid with red phosphorus, and (4) tri-*n*-butyltin hydride with a radical initiator.

Besides the intended reduction, some unfavorable side reactions occurred: methylol ($-CH_2OH$) formation and dehydrobromination yielding a C=C bond (eq 3), as well as lactone formation (eq 2). Side reactions could be identified and estimated through the IR and ^1H NMR spectra of the product copolymers.



$$-CH_2\underset{Br}{CH}-CH_2\overset{CH_3}{\underset{COOCH_3}{C}}- \longrightarrow -CH_2\underset{Br}{CH}-CH_2\overset{CH_3}{\underset{CH_2OH}{C}}- + -CH_2CH{=}CH\overset{CH_3}{\underset{COOCH_3}{C}}- \quad (3)$$

methylol dehydrobromination

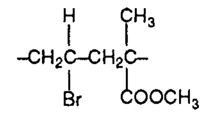
Table III summarizes reduction experiments on the run 9 copolymer of Table I. Sodium cyanoborohydride, which was reported as a selective reducing reagent for a carbon–halogen bond,[8,9] gave the methylol group unexpectedly. Lactone formation also occurred to a large extent, and the intended reduction was not detected. The received sodium cyanoborohydride reagent was extra-pure grade but the supplier (Nakarai Chemicals, Ltd., Kyoto) guaranteed only 95% purity. A possible impurity[9] was sodium borohydride, and although this impurity might be responsible for the methylol formation, this reagent was considered unsuccessful and not studied further.

Sodium hydride, which was described as a dehydrohalogenating reagent for haloesters,[10] brought about 20% of intended reduction, but with 15% dehydrobromination and 35% lactone formation. Figure 3 shows identification of these side reactions as well as intended reduction by spectroscopic methods.

Refluxing with hydroiodic acid in the presence of red phosphorus, with reference to an early study on the reduction of poly(vinyl chloride),[11] gave 39% of intended reduction and ester hydrolysis at the same time. The major reaction (61%), however, was again lactone formation. Attempted lactone ring opening and reduction of the resulting hydroxyl group by further refluxing with an excess of hydroiodic acid was unsuccessful.

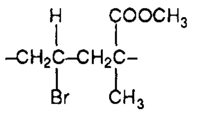
Reduction by using tri-*n*-butyltin hydride, which was applied to the partial reduction of poly(vinyl bromide),[12] seemed hopeful as shown by runs 4–6 of Table III. The only side reaction observed was lactone formation, and it was expected to be suppressed by carrying out the reaction at low temperature. Thus in run 7 all procedures, copolymerization, isolation and drying of the copolymer, and its reduction, were carried out at −20 °C. The reaction with a large excess of tri-*n*-butyltin hydride was initiated by irradiating with a tungsten lamp in the presence of AIBN. With such precautions, a copolymer **2** containing only 2% lactone unit was obtained in 94% yield. Figure 4 shows ^1H NMR and IR spectra of this copolymer sample. Absorptions due to the lactone unit are very weak, as shown, and other absorptions are reasonably assigned to the structure **2**. Figure 5 shows its ^{13}C NMR spectrum. Assignment was carried out by referring to a standard chemical shift table and a DEPT (distortionless enhancement by polarization transfer[13]) spectrum. Two CH_2 absorptions observed instead of three CH_2 groups present in one formal repeating unit strongly support the structure **2**, and hence the alternating structure of the parent vinyl bromide–methyl methacrylate copolymer.

Tacticity of the Copolymers. The ^1H and ^{13}C α-CH_3 NMR absorptions and ^{13}C CHBr and C=O NMR absorptions of vinyl bromide–methyl methacrylate alternating copolymer were all split. These splittings were considered as due to methyl methacrylate centered triad configurations. Tentative assignments and intensity ratios of the clearly split three ^1H and ^{13}C α-CH_3 peaks were as follows. ^1H α-CH_3 absorption: 1.02 ppm (cosyndiotactic, 32.0%), 1.20 ppm (coheterotactic, 56.5%), 1.27 ppm (coisotactic, 11.5%). ^{13}C α-CH_3 absorption: 16.0 ppm (cosyndiotactic, 31.0%), 17.6 ppm (coheterotactic, 58.5%), 21.2 ppm (coisotactic, 10.5%). The coisotacticity, σ, was defined as below; i.e., the probability by which the left diad configuration appeared was defined as coisotactic.



$$-CH_2\overset{H}{\underset{Br}{C}}-CH_2\overset{CH_3}{\underset{COOCH_3}{C}}-$$

σ



$$-CH_2\overset{H}{\underset{Br}{C}}-CH_2\overset{COOCH_3}{\underset{CH_3}{C}}-$$

$1-\sigma$

Assuming a Bernouillian model on the steric course of cross-propagation, an averaged coisotacticity, $\sigma = 0.393$, was calculated from the above intensity ratios.

When this copolymer was reduced by using tri-*n*-butyltin hydride at −20 °C, the product ethylene–methyl methacrylate alternating copolymer showed split peaks of the ^1H α-CH_3, ^{13}C α-CH_3, quaternary C, and C=O NMR absorptions. These splittings were considered as due to methyl methacrylate centered pentads. Jo et al.[14] defined an ϵ-tacticity, which referred to the configura-

Table III
Reduction of Vinyl Bromide–Methyl Methacrylate Alternating Copolymer by Several Reducing Reagents

run	reducing reagent	reagent–copolymer mol ratio	solvent	temp, °C	time, h	reaction %[a] R	reaction %[a] L	reaction %[a] M	reaction %[a] D
1	$NaBH_3CN$	2.6	DMSO	23	50	0	40	27	
2	NaH	10	THF–sulfolane	23	170	20	35		15
3	HI-P	7		130	35	39	61		
4	$(n\text{-}C_4H_9)_3SnH$[b]	1.5	THF	40	27	84	16		
5	$(n\text{-}C_4H_9)_3SnH$[c]	1.5	THF	0	27	86	14		
6	$(n\text{-}C_4H_9)_3SnH$[c]	6.2	THF	−20	36	94	6		
7[d]	$(n\text{-}C_4H_9)_3SnH$[c]	7.7	THF	−20	50	98	2		

[a] R, reduction; L, lactone formation; M, methylol formation; D, dehydrobromination. [b] 17 mol % AIBN based on copolymer was added. [c] 17 mol % AIBN based on copolymer was added, and the mixture was irradiated by a tungsten lamp. [d] All procedures, from copolymerization to reduction, were carried out at −20 °C.

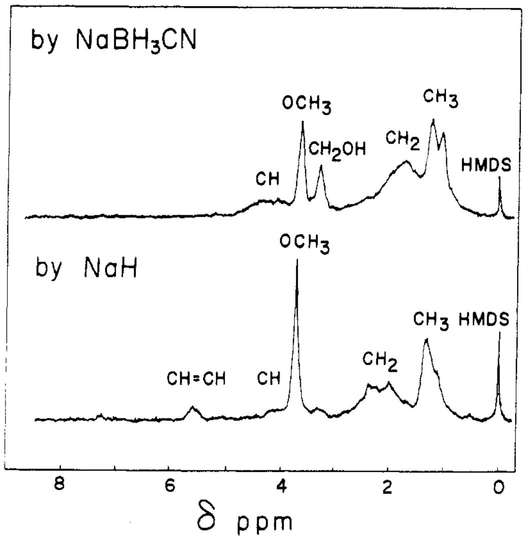


Figure 3. 60-MHz ^1H NMR spectra of reduction reaction products of vinyl bromide–methyl methacrylate alternating copolymer, by $NaBH_3CN$ (above) and by NaH (below).

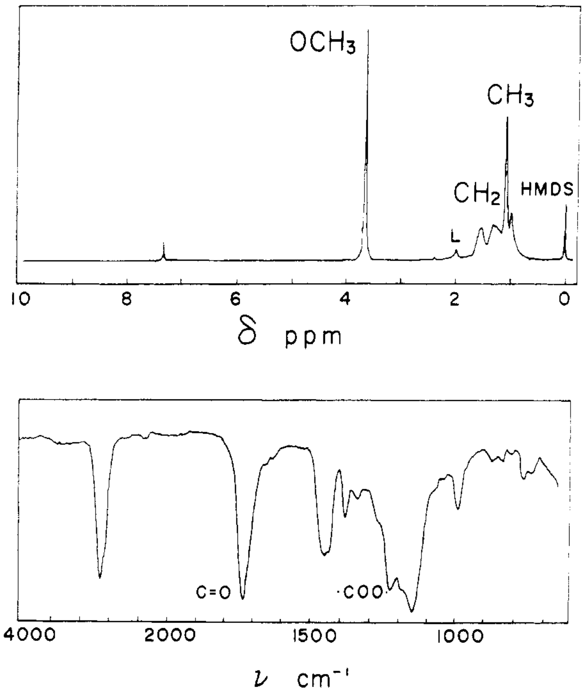


Figure 4. 200-MHz ^1H NMR and IR spectra of ethylene–methyl methacrylate alternating copolymer. Peak L in ^1H NMR spectrum is due to CH_2 group in lactone units. Peak due to lactone CH group is too weak to be observed.

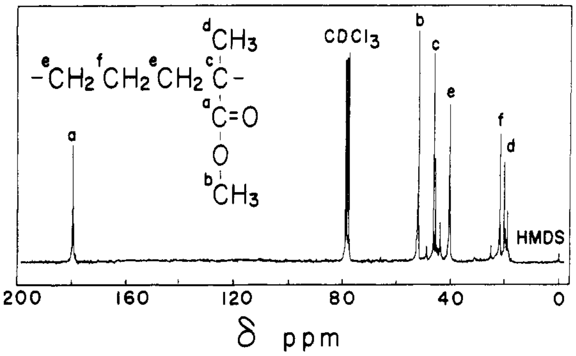
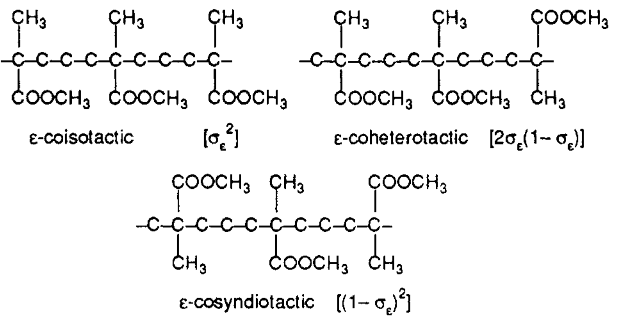
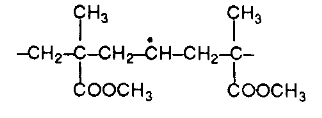


Figure 5. 50-MHz ^{13}C NMR spectrum of ethylene–methyl methacrylate alternating copolymer.

tional relationship between the α-carbon and the ε-carbon. Thus, according to their definition, the below three types of pentad could be designated as ε-coisotactic, ε-coheterotactic, and ε-cosyndiotactic. When we define a probability, σ_ϵ (ε-coisotacticity), by which the two succeeding methacrylate units have the same configuration and again assume a Bernouillian model on the formation of the pentads, their fractions will be given by the equations in the brackets.



From the split peak intensity ratios of ^{13}C quaternary C and C=O absorptions, an averaged σ_ϵ could be calculated to be 0.230. Assignments and intensity ratios were as follows. Quaternary C absorption: 44.8 ppm (ε-coisotactic, 10.1%), 46.0 ppm (ε-coheterotactic, 27.4%), 46.8 ppm (ε-cosyndiotactic, 62.5%). C=O absorption: 179.6 ppm (ε-cosyndiotactic, 62.1%), 179.8 ppm (ε-coheterotactic, 28.8%), 180.0 ppm (ε-coisotactic, 9.1%). In the course of tin hydride reduction, rotation of the main-chain C–C bonds of a radical intermediate


$$-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-CH_2-\dot{C}H-CH_2-\underset{COOCH_3}{\overset{CH_3}{C}}-$$

occurred so as to place the two polar $-COOCH_3$ groups apart and gave the ε-coisotacticity = 0.230. Retention or inversion at the reaction site does not give such a value.

Copolymer Properties. The ethylene–methyl methacrylate alternating copolymer obtained above (run 7, with 2% lactone unit) had a number-averaged molecular weight of 32 000 and a weight-averaged molecular weight of 48 000 as determined by GPC with reference to polystyrene standards. Another sample of copolymer **3** with a number-averaged molecular weight of 24 000 (a degree of polymerization of 116) gave a copolymer **2** with a number-averaged molecular weight of 14 000 (a degree of polymerization of 109) after the reduction. Thus no significant degradation occurred during the tin hydride reduction. The copolymer **2** formed a transparent soft and rubbery film. It was soluble in chloroform, benzene, acetone, THF, and *N*,*N*-dimethylformamide. A cooling DSC experiment showed no crystallization peak but showed a glass transition temperature at 19 °C. Ethylene–ethylene–methyl methacrylate periodic copolymer (**1**) in the previous paper[1] was partially crystalline and had a glass transition temperature of 45 °C.

References and Notes

(1) Yokota, K.; Hirabayashi, T. *Macromolecules* **1981**, *14*, 1613.
(2) Yokota, K.; Kougo, T.; Hirabayashi, T. *Polym. J.* **1983**, *15*, 349.
(3) Logothetis, A. L.; McKenna, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1976**, *17*, 642.
(4) Hirooka, M.; Yabuuchi, H.; Kawasumi, S.; Nakaguchi, K. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 1281.
(5) Hirabayashi, T.; Yokota, K., to be published.
(6) Flory, P. J. *J. Am. Chem. Soc.* **1938**, *61*, 1518.
(7) Hirabayashi, T.; Yokota, K. *Polym. J.* **1981**, *13*, 51.
(8) Buehler, C. A.; Pearson, D. E. *Survey of Organic Syntheses*; John Wiley & Sons, Inc.: New York, 1977; Vol. 2, p 9.
(9) Hutchins, R. O.; Maryanoff, B. E.; Milewski, L. A. *J. Chem. Soc. D* **1971**, 1097.
(10) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; John Wiley & Sons, Inc.: New York, 1967; p 1078.
(11) Staudinger, H.; Brunner, M.; Feisst, W. *Helv. Chim. Acta* **1930**, *13*, 805.
(12) Cais, R. E.; Kometani, J. M. *Macromolecules* **1982**, *15*, 954.
(13) Pegg, D. T.; Doddrell, D. M.; Bendall, M. R. *J. Chem. Phys.* **1982**, *77*, 2745.
(14) Jo, Y. S.; Inoue, Y.; Chûjô, R.; Saito, K.; Miyata, S. *Macromolecules* **1985**, *18*, 1850.

Synthesis of Polymers with Amino End Groups. 3. Reactions of Anionic Living Polymers with α-Halo-ω-aminoalkanes with a Protected Amino Functionality

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ABSTRACT: Well-defined polymers amino functionalized at their chain ends were synthesized by the reactions of either anionic living polystyrenes or polyisoprenes with α-halo-ω-aminoalkanes with a protected amino functionality. The reactions generally proceeded well in THF at −78–25 °C to afford the aminated polymers in good yields. Careful analyses of the resulting polymers by a combination of acid–base titration ($HClO_4$), size-exclusion chromatography (SEC), and thin-layer chromatography (TLC) indicated that these polymers had high degrees of amination (>95%) at their end groups as well as predictable molecular weights and narrow molecular weight distributions. The usefulness of applying the TLC/flame ionization detection technique to quantitative analysis of the resulting polymers was discussed.

Introduction

The synthesis of chain end functionalized polymers (or the so-called telechelic polymers) is still of great interest because they have practically and potentially numerous applications. Anionic living polymerization is the preferred method for preparing such polymers because it leads to predictable polymer molecular weights and narrow molecular weight distributions. Many possible end functionalizations of anionic living polymers have been reported and well reviewed.[1-7] Widely studied and successful examples are hydroxyl and carboxyl end functionalized polymers that can be synthesized by the reaction of an anionic living polymer with either ethylene oxide[8-11] or carbon dioxide.[12-15] The resulting polymers have well-defined structures (e.g. molecular weight and molecular weight distribution as well as degree of end functionalization).

On the other hand, a general method for introducing primary amino groups to the terminals of living polymer has not been well established yet, although a couple of new methods have been reported so far. For example, Schulz and Halasa prepared the polyisoprenes and poly(1,3-butadienes) with amino groups at their polymer chain ends by using the initiator *p*-lithio-*N*,*N*-bis(trimethylsilyl)aniline which had a primary amine protected group.[16] The method appeared to be excellent for preparation of mono aminated polymers. However, it is relatively difficult to prepare aminated polymers at both chain ends by this system because they are prepared only by the coupling reaction which requires a very high precision in the stoichiometry of the living polymer and coupling agent, e.g. dimethylsilane dichloride.

We have recently developed a new aminating reagent, *N*-(phenylmethylene)trimethylsilanamine, which reacts efficiently with a variety of organolithium compounds to

0024-9297/90/2223-0939$02.50/0