Anionic Copolymerization of α-Methylstyrene and 2, 3-Dimethylbutadiene

Heimei Yuki, Yoshio Okamoto, Hidekazu Takano, and Koji Ohta

Department of Chemistry, Faculty of Engineering Science, Osaka University, Toyonaka, Osaka, Japan.

ABSTRACT: α-Methylstyrene(α-MeSt) and 2, 3-dimethylbutadiene (DMB) were copolymerized in THF and in hydrocarbon solvents with *n*-BuLi. The copolymer produced at 60°C in THF was composed of almost equimolar amounts of α-MeSt and DMB, if α-MeSt was charged in excess. In the copolymer α-MeSt and DMB were considered to be arranged alternately, and DMB was incorporated in the form of 1, 4-structure. In the copolymerization below 60°C the copolymer composition was affected by the ratio of initial monomer concentrations. The content of α-MeSt in the copolymer increased with decreasing polymerization temperature and reached 91% at −78°C. The copolymerization at 30°C gave the copolymer composed of (2 : 1) α-MeSt and DMB under the existence of large excess of α-MeSt. It was presumed that the major part of the copolymer was composed of repeated sequences of [α-MeSt·α-MeSt·DMB]. In benzene a copolymer rich in DMB (71%) was obtained at 60°C. The addition of THF to the polymerization system in benzene decreased the content of DMB.

KEY WORDS Anionic Copolymerization / α-Methylstyrene / 2, 3-Dimethylbutadiene / Alternating Copolymer / NMR /

The authors have reported the anionic alternating copolymerizations[1] including 1, 1-diphenylethylene[2] or *trans*-stilbene[3] (M_2), which can not alone be polymerized. The comonomers (M_1) combined with M_2 were styrene, some substituted styrenes and conjugated dienes such as butadiene, isoprene and 2, 3-dimethylbutadiene. α-Methylstyrene (α-MeSt) can not be homopolymerized above 61°C because of the low ceiling temperature.[4] Therefore, α-MeSt will be a candidate of the monomer M_2 in such an alternating copolymerization as those described above, if a suitable comonomer M_1 is chosen as the propagation rate constant k_{12} being larger than k_{11} and the polymerization reaction is conducted above 60°C.

There seems to be very few reports on the anionic copolymerization including α-MeSt as one of the comonomers. Szwarc and his coworkers have studied and determined the rate constants of the reactions between living polystyrene and α-MeSt monomer[5] and also between living poly-α-MeSt and a number of styrene derivatives[6] in THF. Tölle, *et al.*,[7], have studied the anionic copolymerization of α-MeSt and styrene in THF and determined the monomer reactivity ratios around room temperature. The polymer produced in the copolymerization was considered to have such a tapered structure that a sequence composed of styrene units at one end changes continuously into that of alternating units of styrene and α-MeSt at the other end in the molecule, because the reaction mixture forms a living system and the reactivity of styrene toward anion is higher than that of α-MeSt.

In the previous paper[8] we reported the anionic polymerization of 2, 3-dimethylbutadiene (DMB) and proposed that the polymer produced above −30°C in THF was composed of alternating units of 1, 2- and 1, 4-structure. The 1, 2-structure of DMB is sterically very similar to the structure of α-MeSt unit. In this paper the results of the anonic copolymerization of α-MeSt and DMB are reported.

EXPERIMENTAL

Materials

2, 3-Dimethylbutadiene was synthesized by the

dehydration of pinacol as described by Allen.[9] The monomer boiling at 69.5°C (760 mm) was dried over lithium aluminum hydride and distilled *in vacuo* before use.

α-Methylstyrene was distilled under reduced pressure. The purified monomer was dried with lithium aluminum hydride and distilled *in vacuo* before use.

n-Butyllithium (*n*-BuLi) was prepared in *n*-heptane according to the method of Ziegler[10] from *n*-butyl chloride and metallic lithium.

Tetrahydrofuran (THF) was first refluxed over metallic sodium and then over lithium aluminum hydride. This was distilled onto Na-K alloy and naphthalene. From the green solution the solvent was transferred to a reaction vessel on a vacuum line just before use.

Benzene and *n*-heptane were purified by the useal methods and were stored over sodium. Before use, each of the solvents was transferred to a flask containing a small amount of *n*-BuLi in *n*-heptane and then distilled under high vacuum.

Polymerization

Using a vacuum system, a solvent was first transferred to a glass ampoule which had been evacuated and baked with a gas burner. Then the monomers and an initiator were added with hypodermic syringes to the ampoule, which was held in a thermostat, under dry nitrogen. The ampoule was sealed and the reaction was allowed to proceed. After the reaction was terminated by adding a small amount of methanol, the reaction mixture was poured into a large amount of methanol. The precipitated polymer was filtered, washed with methanol and dried. The polymer was stored at −20°C.

Measurements

The NMR spectrum of the polymer was measured at 60°C with a JNM-4H-100 spectrometer at 100 MHz by using carbon tetrachloride as a solvent. The concentration of the sample was ca. 10% (w/v). The chemical shifts are refered to the signal of tetramethylsilane used as an internal standard. A small amount of methylene dichloride was added to the sample solution and its signal was used as a lock signal.

The solution viscosity of the polymer was determined in toluene at 30 ± 0.03°C, the concentration of the polymer being 0.5g/dl.

RESULTS

The anionic copolymerization of DMB (M_1) and α-MeSt (M_2) was carried out with *n*-BuLi in THF at $[M_2]_0 > [M_1]_0$ where $[M_2]_0$ and $[M_1]_0$

Table I. Anionic copolymerization of α-methylstyrene (M_2) and 2, 3-dimethylbutadiene (M_1)[a]

| No. | $[M_2]_0/[M_1]_0$, mol/mol | Temp, °C | Time, hr | Polymer | | | | |
| | | | | Yield, % | M_1 content, mol % | | η_{sp}/c,[d] dl/g | sp,[e] °C |
					I[b]	II[c]		
1	3.62	60	0.5	46.1	44.2	46.9	0.22	—
2	3.09	60	0.5	55.5	—	44.1	0.17	98~108
3	3.05	60	0.5	52.1	45.4	47.4	0.23	100~111
4	2.96	60	0.5	56.0	—	45.1	0.13	—
5	2.39	60	0.5	61.6	—	47.8	0.22	100~110
6	1.50	50	2.5	81.8	49.0	49.0	0.30	—
7	3.06	30	24.0	68.8	36.5	35.9	0.39	125~135
8	1.48	30	18.0	92.2	—	43.7	0.32	—
9	3.02	0	24.0	93.3	26.1	26.6	0.43	108~120
10	1.54	0	18.0	98.8	40.3	39.4	0.26	—
11	1.08	−78	20.0	37.5	8.5	—	—	—

[a] $[M_1]_0$, 4.0~4.3 mmol; solvent, THF 15 ml; initiator, *n*-BuLi 0.064 mmol.
[b] Determined from NMR spectrum. [c] Determined from polymer yield.
[d] Toluene solution at 30°C, $c=0.50$ g/dl. [e] sp, softening point.

are the initial monomer concentrations. The results are shown in Table I. The copolymerization at 60°C was rather fast. In order to check the consumption of the monomers in this polymerization a control experiment was performed. After a reaction period of 30 min, the volatile fraction was collected from the reaction mixture by vacuum distillation, and the fraction was examined by gas chromatography. The result indicated that DMB was completely consumed in the polymerization. It was also found that 18 hours suffice for the complete consumption of DMB in the copolymerization at 30 and 0°C

Figure 1. NMR spectra of poly-α-MeSt (A) and copolymers of α-MeSt and DMB (B, C, D): (A) prepared in THF by Naph-Na at -78°C; (B) prepared in THF by n-BuLi at 30°C; DMB content, 33%; (C) prepared in THF by n-BuLi at 50°C; DMB content, 49%; (D) prepared in benzene by n-BuLi at 60°C; DMB content 71%. The spectrum (D) was measured in the absence of methylene dichloride using the signal of tetramethylsilane as a lock signal.
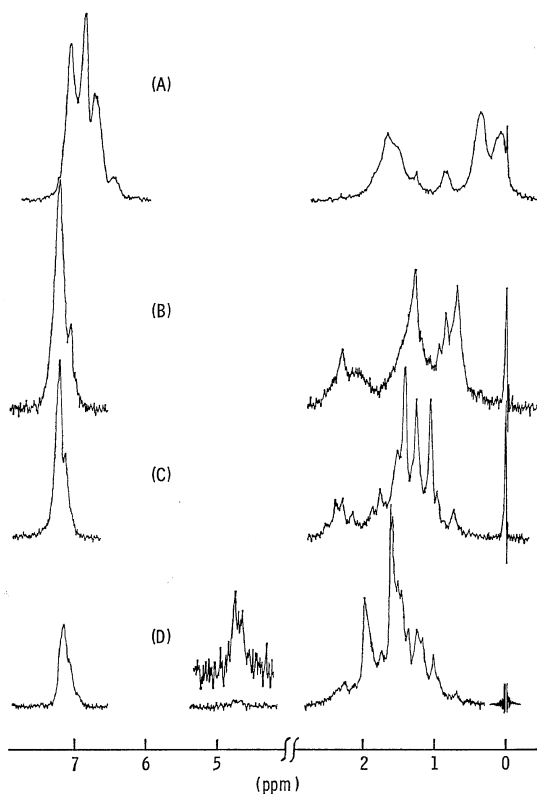
under the reaction conditions employed. Thus the composition of the copolymer can be calculated from the initial monomer concentrations and the polymer yield.

The NMR spectrum of the copolymer prepared in THF with n-BuLi at 50°C is shown in Figure 1, as an example. The copolymer composition was also calculated from the intensity ratio of the peaks of phenyl protons (7.0—7.4 ppm) to the others. Both the values obtained from polymer yield and from NMR spectrum were in good agreement and within experimental error, as shown in Table I.

The copolymers produced at 60°C were composed of almost equimolar amounts of M_1 and M_2, when the ratio $[M_2]_0/[M_1]_0$ was 2.4—3.6. On the other hand, in the copolymerization below 60°C, not only the content of α-MeSt in the copolymer increased, but also the copolymer composition became strongly affected by the ratio of initial monomer concentrations, with decreasing polymerization temperature. At -78°C the DMB content was only 8.5% in the polymer formed from equimolar concentrations of M_1 and M_2.

The copolymerization in THF was carried out at 30°C under various ratios of initial monomer concentrations, where $[M_1]_0$ was kept constant. The results are shown in Table II. At $[M_2]_0/[M_1]_0=1.5$ the M_1 content in the polymer was 44%. With increasing $[M_2]_0/[M_1]_0$, the M_1 content decreased gradually and reached about 33%, i.e., the polymer was composed of 2 : 1 molar ratio of α-MeSt and DMB, at $[M_1]_0/[M_1]_0=3$. When the copolymerization was carried out at high, but constant ratio of initial monomer concentrations ($[M_2]_0/[M_1]_0=10$) and the total monomer concentration varied, the M_1 content in the polymer increased with a decrease in the monomer concentration as shown in Table II. However, it must be noted that in these copolymerizations, in spite of the presence of large excess α-MeSt, the α-MeSt content of the most copolymers lies around two moles against one mole of DMB, leaving large amount of α-MeSt unreacted.

The NMR spectra of all the polymers obtained in THF showed no absorption peak due to the olefinic protons in 1, 2-structure of DMB.

Table II. Anionic copolymerization of α-methylstyrene (M$_2$) and 2, 3-dimethylbutadiene (M$_1$) in THF by n-BuLi at 30°C[a]

No.	[M$_2$]$_0$, mmol	[M$_1$]$_0$, mmol	[M$_2$]$_0$/[M$_1$]$_0$, mol/mol	Polymer		
				Yield, %	M$_1$ content,[b] mol %	η_{sp}/c,[c] dl/g
8	6.32	4.27	1.48	92.2	43.7	0.32
12	10.30	4.40	2.34	75.1	38.0	0.23
13	13.44	4.31	3.12	70.1	34.6	0.22
14	15.61	4.30	3.63	62.9	34.3	0.22
15	17.68	4.42	4.00	60.0	32.1 (33.3)	0.22
16	22.03	4.45	4.95	52.4	32.1	0.22
17	30.49	4.35	7.01	43.0	29.0	0.22
18	8.99	0.88	10.22	24.6	33.5 (37.5)	—
19	10.00	1.00	10.00	24.8	33.9 (36.1)	0.17
20	19.66	2.05	9.59	29.4	30.0 (33.3)	0.24
21	21.98	2.00	10.99	26.0	29.9 (32.3)	—
22	38.96	3.94	9.89	34.2	25.5 (24.6)	0.30
23	44.06	4.18	10.54	34.7	23.8 (26.3)	0.24

[a] THF, 15 ml; n-BuLi, 0.064 mmol; time, 18 hr.
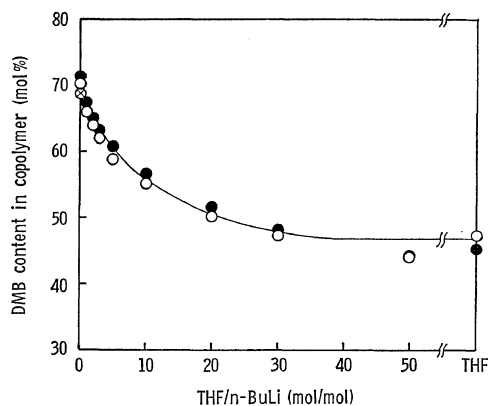[b] Determined from polymer yield. The values in parentheses were those measured by NMR spectroscopy.
[c] Determined in toluene solution at 30°C, $c=0.5$ g/dl.

When the copolymerization was performed in hydrocarbon solvents with n-BuLi at 60°C, DMB was predominantly incorporated in the polymer. The addition of a small amount of THF to the reaction mixture in benzene resulted in a sharp decrease in the DMB content. However, thirtyfold excess of THF to n-BuLi used was required to give such alternating copolymer

Figure 2. Composition of copolymer prepared with addition of THF at 60°C: ○, determined from polymer yield (⊗, in toluene); ●, determined from NMR spectrum.
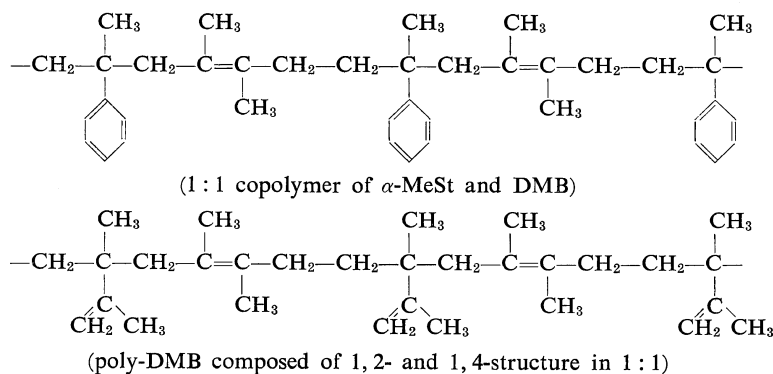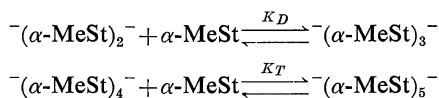
as that obtained in THF. The results are shown in Figure 2. The major part of the DMB units in the copolymer prepared in benzene was 1, 4-structure, but a weak absorption of olefinic protons in the 1,2-structure also appeared at 4.75 ppm in the spectrum of this polymer.

DISCUSSION

α-MeSt anion is unable to add to α-MeSt monomer at 60°C because of the ceiling temperature, but it could be nevertheless copolymerized rapidly with DMB even at 60°C in THF producing a polymer composed of 1 : 1 molar ratio of α-MeSt and DMB. In the copolymerization DMB was consumed completely, leaving a large excess of unreacted α-MeSt. These facts indicate that this polymer must be the alternating copolymer. In the copolymer DMB unit had only 1, 4-structure, which can release the steric hindrance between neighboring α-MeSt units. This is compatible with the finding that the anionic polymerization of DMB in THF gives a polymer consisting of 1,2- and 1,4-units arranged alternately,[8] where the structure of the 1,2-unit is similar to that of α-MeSt unit in the present copolymer.

(1 : 1 copolymer of α-MeSt and DMB)

(poly-DMB composed of 1, 2- and 1, 4-structure in 1 : 1)

In the NMR spectrum of poly-α-MeSt (Figure 1) the resonance peaks of α-methyl protons appeared at 0.10, 0.38 and 0.85 ppm and those of phenyl protons at 6.5—7.3 ppm. On the other hand, the NMR spectrum of the copolymer showed the absorption of phenyl protons at 6.9—7.4 ppm and no absorption at 0.1—0.5 ppm, where α-methyl protons of poly-α-MeSt resonate. The upfield shifts of the resonances of the monomeric unit in poly-α-MeSt are explained by the influences of benzene rings in the neighboring monomeric units.[11] Therefore, the downfield shifts of the spectrum of the copolymer compared with the spectrum of poly-α-MeSt imply that the monomeric units of α-MeSt were not continuously arranged in the copolymer.

The results of the copolymerization shown in Table I indicate that α-MeSt is more reactive to carbanion than DMB, i.e., $k_{12} > k_{11}$ in THF at the temperature range tested. It is also well known that the addition of α-MeSt to both ends of the living tail-to-tail dimer proceeds much faster than the further growth of the resulting tetramer.[12] The equilibrium constants at 25.4°C in the reactions,

$$^-(\alpha\text{-MeSt})_2{}^- + \alpha\text{-MeSt} \xrightleftharpoons{K_D} {}^-(\alpha\text{-MeSt})_3{}^-$$

$$^-(\alpha\text{-MeSt})_4{}^- + \alpha\text{-MeSt} \xrightleftharpoons{K_T} {}^-(\alpha\text{-MeSt})_5{}^-$$

have been determined as $K_D = 240 \pm 30$, $K_T = 9.4$ (at 0°C)* and $K_\infty = 0.41$ $l\,\text{mol}^{-1}$, where K_∞ refers to high molecular weight polymer.[13] These data suggest that in the polymerization initiated with monoanion such as n-BuLi, α-MeSt can form the dimer, but further growth encounters increasing difficulty in the vicinity of room temperature and at a usual monomer concentration. Thus, the formation of 2 : 1 copolymer of α-MeSt and DMB in the copolymerization at 30°C (Table II) is correlated with the reactivity of α-MeSt anion at the growing chain end. From the above considerations, it may be very likely that the major part of the 2 : 1 copolymer is composed of repeated sequences of [α-MeSt·α-MeSt·DMB] as follows.
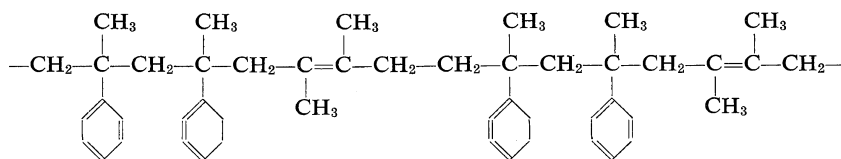
It must be noted, however, that the copolymer compositions varied with the total initial monomer concentrations even if the ratio $[M_2]_0/[M_1]_0$ was almost constant in the copolymerization at 30°C (Table II), because the concentration of α-MeSt affects the equilibrium in the reaction described above.

* The value was obtained for the tetramer dianion whose structure was tail-to-tail, head-to-head, and tail-to-tail.

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