Anionic Copolymerizations of 1,1-Diphenylethylene with o- and p-Methoxystyrene

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ABSTRACT: Anionic copolymerizations of 1,1-diphenylethylene (DPE) with o- and p-methoxystyrene (o- and p-MeOSt) were investigated with n-butyllithium (n-BuLi) and other anionic initiators. In THF, alternating copolymers of DPE with o- and p-MeOSt were obtained. In aromatic hydrocarbons, the copolymerization of DPE and o-MeOSt with n-BuLi gave a polymer having higher o-MeOSt content, while an almost alternating copolymer was obtained in the copolymerization of DPE and p-MeOSt. The NMR spectra of the alternating copolymers of DPE with o- and p-MeOSt showed the splittings due to the tactic difference with respect to the methoxy group. The latter alternating copolymer was shown by polarized light and X-ray examinations to be crystalline.

KEY WORDS   Anionic Copolymerization / 1,1-Diphenylethylene / o-Methoxystyrene / p-Methoxystyrene /

In earlier studies anionic coplymerizations of various monomer pairs were carried out to obtain information on the reactivities of the monomers and to form new polymers,[1-5] some of which were alternating. On the other hand, o-methoxystyrene (o-MeOSt) formed a crystalline isotactic polymer in a nonpolar solvent by means of n-butyllithium (n-BuLi), but formed an atactic polymer in tetrahydrofuran (THF)[6] It was supposed that the driving force behind the formation of the isotactic poly (o-methoxystyrene) (P-o-MeOSt) was the interactions of the ether oxygens of the monomer and/or the polymer with lithium counter-ion, and the interactions were diminished in a solvent of higher solvating power such as THF.

It is probable that the interaction stated above may occur in the copolymerization of o-MeOSt and 1,1-diphenylethylene (DPE), and greatly affect the reactivity. In the present paper, besides the copolymerization of these two monomers, the copolymerization of p-methoxystyrene (p-MeOSt) and DPE is also studied in order to know the properties of the copolymer and the reactivity of the isomer.

EXPERIMENTAL

Materials

  o-MeOSt

This was synthesized by dehydration of methyl-(2-methoxyphenyl)carbinol over acid potassium sulfate at 220–230°C,[6] and then the crude product was fractionally distilled. The monomer was dried over lithium aluminum hydride in an atmosphere of dry nitrogen, from whence it was redistilled, bp 80–81°C (10 mmHg), n_D^{20} 1.5605. No impurity was detected by gas chromatography or NMR spectroscopy.

  p-MeOSt

p-MeOSt was obtained by distillation of methyl-(4-methoxyphenyl)carbinol in the presence of a small amount of hydrochloric acid. The monomer purified by distillation was dried over lithium aluminum hydride and redistilled, bp 85°C (13 mmHg), n_D^{20} 1.5615. No impurity was detected by gas chromatography or NMR spectroscopy.

  DPE

This was prepared by dehydration of methyl-diphenylcarbinol with sulfuric acid.[7] The monomer was first stirred with Na-K alloy, and then n-BuLi in n-heptane was added until a red coloration appeared. The colored solution was fractionally distilled under dry nitrogen. The fraction of bp 97–98°C (1.5 mmHg) was collected; n_D^{20} 1.6085.

  THF

The solvent refluxed over lithium aluminum hydride was distilled onto benzophenone and

Na–K alloy. The solvent was then distilled *in vacuo* from the blue solution before use.

Benzene and Toluene

Each solvent purified in the usual manner was mixed with *n*-BuLi prepared in the same solvent, and was distilled under high vacuum before use.

n-BuLi

The initiator was prepared in *n*-heptane according to the method of Ziegler.[8]

Na-Naphthalene, Na- and K-dispersions

Na-naphthalene was synthesized in THF; Na- and K-dispersions were prepared in *n*-heptane.

Polymerization

Polymerization was carried out in a dry glass ampoule under dry argon. Solvent was first transferred to the ampoule on a vacuum line, and then monomers and an initiator were added by using syringes. The initiator was added dropwise until the red color due to monomer anions became stable; usually *ca.* 0.012 mmol of the initiator was required for a 15 m*l* solution. Then an additional 0.060 mmol of the initiator was added. After the polymerization was terminated by a small amount of methanol, the mixture was poured into methanol. The precipitated polymer was filtered, washed with methanol, dried, and weighed. On the other hand, the mother liquor of the polymer precipitation was evaporated under reduced pressure. The composition of the monomer mixture recovered from the above residue was determined from the refractive index.

Measurement

NMR Spectrum

The spectrum was taken on a JNM–4H–100 (Japan Electron Optics Laboratory Co. Ltd.) at 100 MHz in carbon tetrachloride or in chloroform by using tetramethylsilane as an internal standard, the temperature of the run being 60°C.

X-ray Diffraction

The X-ray diffraction was measured with a Rigakudenki 4001 X-ray Diffractometer (CuKα-radiation).

Viscosity

The solution viscosity of the polymer was measured in chloroform at 25.0°C; the concentration was 1.0 g/d*l*.

Reaction of the Copolymer with Hydriodic Acid

In order to assign the position of the methoxy group in the NMR spectrum of the alternating *o*-MeOSt–DPE copolymer, the conversion of the methoxy group to a hydroxy group was tried through a reaction of the copolymer with hydriodic acid.[9] The copolymer (0.30 g) and 56% hydriodic acid (6 m*l*) were heated in glacial acetic acid (6 m*l*) at 120–130°C. After 6 hours, the reaction mixture was poured into a large amount of methanol. The precipitated polymer was filtered, washed with methanol, and dried. The polymer was then reprecipitated twice from benzene-methanol and a colorless powder was recovered.

Anal. Calcd. for alternating *o*-MeOSt–DPE copolymer: C, 87.86; H, 7.05. Calcd. for alternating *o*-hydroxystyrene–DPE copolymer: C, 87.96; H, 6.71, Found: 87.43; H, 6.92.

RESULTS

The results of the copolymerization of *o*-MeOSt (M$_1$) and DPE (M$_2$) in THF are shown in Table I. Copolymer composition was determined by elementary analysis and from the relative intensity of signals of aromatic and aliphatic protons in the NMR spectrum. In all cases the composition

Table I. Anionic copolymerization of *o*-MeOSt (M$_1$) and DPE (M$_2$) in THF[a]

Initiator 0.06 mmol	[M$_1$]$_0$/[M$_2$]$_0$ (mol/mol)	Time (day)	Yield (wt%)	[m$_1$]/[m$_2$] E.A.[b]	NMR[c]	[η] (d*l*/g)
n-BuLi	0.953	16	77.3	1.0	—	—
n-BuLi	0.909	9	73.4	0.9	1.1	0.10
n-BuLi	0.826	16	77.6	1.0	—	—
n-BuLi	0.350	13	48.5	1.0	1.0	—
Na-naph.	0.909	16	71.4	1.0	—	0.15
K-disp.	0.909	16	52.3	1.1	1.1	0.15

[a] [M$_1$]$_0$ 3.67 mmol, THF 15 m*l*, Temp. 0°C
[b] Copolymer composition determined by elementary analysis.
[c] Copolymer composition determined by NMR spectroscopy.

Table II. Anionic copolymerization of o-MeOSt (M₁) and DPE (M₂)
in aromatic hydrocarbon by n-BuLi[a]

Solvent 15 ml	M_1 (g)	M_2 (g)	Temp. (°C)	Time (day)	Polymer (g)	Recovered[b] monomer (g)	n_D^{20}[c]
Toluene	0.494	0.739	−30	14	0.609	0.616	1.6080
Toluene	0.522	0.813	0	13	0.611	0.725	1.6070
Benzene	0.494	0.718	40	8	0.593	0.584	1.6078

[a] [n-BuLi] 0.06 mmol
[b] Contained ca. 5 mg of lithium compounds.
[c] Refractive index of the recovered monomer.

Table III. Anionic copolymerization of o-MeOSt (M₁) and DPE (M₂) in aromatic hydrocarbon[a]

Solvent 15 ml	$[M_1]_0/[M_2]_0$ (mol/mol)	Temp. (°C)	Time (day)	Yield (wt%)	$[m_1]/[m_2]$ Yield[b]	$[m_1]/[m_2]$ E.A.	$[m_1]/[m_2]$ NMR	r_1	$[\eta]$ (dl/g)
Toluene	0.862	−30	13	45.7	7.9	7.5	8.0	29	0.14
Toluene	0.714	−30	14	42.0	6.5	6.5	—	27	—
Toluene	0.893	0	14	49.3	5.8	6.3	7.2	22	0.09
Toluene	0.641	0	16	41.3	4.8	4.8	—	18	—
Toluene[c]	0.357	0	5	22.2	—	1.3	1.6	—	—
Toluene[d]	0.894	20	25	67.5	2.0	1.7	—	—	—
Toluene[d]	0.819	20	25	64.5	1.9	1.7	1.5	—	—
Benzene	0.925	40	8	48.9	6.7	6.2	7.8	20	0.09
Benzene	0.820	40	8	46.0	6.3	6.7	—	20	—

[a] [M₁] ca. 3.8 mmol, Initiator n-BuLi 0.06 mmol
[b] Copolymer composition determined from the polymer yield.
[c] This contained 3% of THF.
[d] Na-dispersion was used as an initiator.

ratio were nearly unity, showing that the copolymers were alternating. Although the color of the polymerization system sustained for a prolonged time, not only DPE but also o-MeOSt remained partially unchanged in the system.

The results of the copolymerizations in aromatic hydrocarbons are shown in Tables II and III. The refractive index of the recovered monomer mixture was approximately the same as that of DPE (Table II), indicating that in these copolymerizations, o-MeOSt was almost completely incorporated into the copolymer. Therefore, the copolymer composition could also be obtained from the polymer yield; the values are in accord with those derived from two other methods, elementary analysis and NMR spectroscopy, as are shown in Table III. The copolymers had a higher o-MeOSt content except for the copolymer with Na-dispersion. In toluene, the copolymer composition, $[m_1]/[m_2]$, at −30°C was greater than that at 0°C, suggesting that the reactivity of o-MeOSt was higher at low temperature. The addition of

a small amount of THF steeply increased the incorporation of DPE. Since the M₁ monomer was completely consumed, the monomer reactivity ratio, r_1, is easily calculated by means of the integrated Mayo-Lewis copolymerization equation;[1] the values are shown in Table III.

The copolymerizations of p-MeOSt (M₁) and DPE (M₂) were carried out in THF and aromatic hydrocarbons with n-BuLi. The results are listed in Table IV. The yield of the copolymer was low even after a prolonged time, and the polymer was clearly precipitated during the polymerization in both THF and toluene, especially in the former. The copolymer composition ratio was nearly unity in THF and aromatic hydrocarbons. The alternating copolymer obtained in THF was crystalline under a polarizing microscope, the X-ray diffraction pattern being shown in Figure 1. The melting point of the crystalline copolymer was 180–185°C. It was soluble in chloroform and partially soluble in carbon tetrachloride.

Table IV. Anionic copolymerization of p-MeOSt (M_1) and DPE (M_2) by n-BuLi[a]

Solvent 15 ml	$[M_1]_0/[M_2]_0$ (mol/mol)	Time (day)	Yield (wt%)	$[m_1]/[m_2]$[b]		$[\eta]$ (dl/g)
				E.A.	NMR	
THF	0.971	16	35.6	1.0	1.0	—
THF	0.885	17	33.1	1.0	—	—
THF	0.827	17	31.5	1.0	1.0	0.14
Toluene	0.901	14	11.9	1.2	—	0.06
Toluene	0.747	16	11.1	1.2	1.2	—
Benzene[c]	0.918	8	9.6	1.2	1.1	—
Benzene[c]	0.769	8	7.4	1.2	—	—

[a] ($[M_1]_0$ 3.97 mmol, [n-BuLi] 0.06 mmol)
[b] Copolymer compositions determined by elementary analysis and NMR spectroscopy.
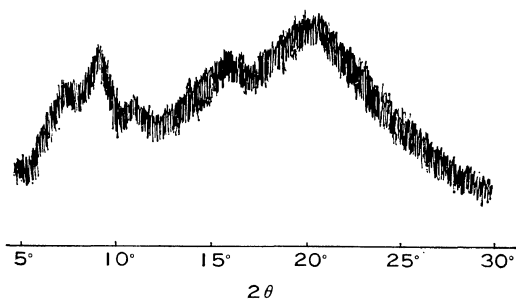[c] Temp. 40°C

Figure 1. X-ray pattern of the alternating copolymer of p-MeOSt and DPE.

The NMR spectrum of the alternating copolymer of o-MeOSt and DPE is shown in Figure 2. Based on the area intensity of the spectrum, the peaks at 2.75, 2.85, and 3.39 ppm were assigned to the methoxy group. The NMR spectrum of the polymer which had been treated with hydriodic acid showed that only the peaks at 2.75, 2.85 and 3.39 ppm were diminished by $ca.$ 20% compared with other peaks. The IR spectrum of the polymer treated with hydriodic acid showed an absorption due to a hydroxy group at 3300 cm^{-1}. These results indicate that the assignment of the methoxy group is correct. In the NMR spectrum of P-o-MeOSt which was prepared under the same reaction conditions as the alternating copolymer, methoxy resonance was found at 3.03–3.40 ppm.[6] No peak was, however, observed at 3.05–3.25 ppm in Figure 2, indicating that the alternating copolymer had no continuous unit of o-MeOSt.

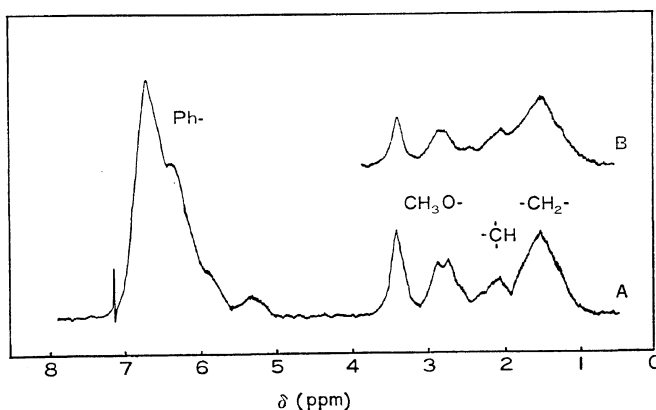The NMR spectrum of the alternating copolymer of p-MeOSt and DPE is shown in Figure 3.

Figure 2. A: NMR spectrum of the alternating copolymer of o-MeOSt and DPE.
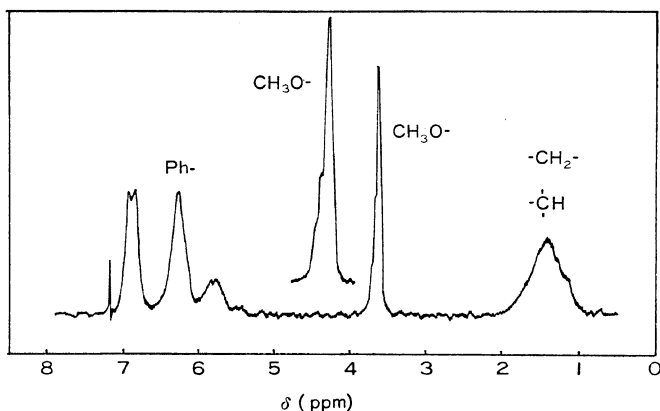B: NMR spectrum of the copolymer obtained by treating the above copolymer with hydriodic acid. (in CDCl$_3$).

Figure 3. NMR spectrum of the alternating copolymer of p-MeOSt and DPE (in $CDCl_3$).

A narrow peak of the methoxy group was observed at 3.61 ppm, but it also seemed to be composed of three components. The methoxy resonances of poly-p-MeOSt which was polymerized in THF and benzene with n-BuLi appeared at 3.75 ppm as a narrow peak.

DISCUSSION

As DPE cannot be homopolymerized, the following results indicate that the copolymers of DPE with o- and p-MeOSt prepared in THF were alternating; *i.e.*, the copolymer composition was 1 : 1 and no peaks due to the continuous units of o- and p-MeOSt were observed in the NMR spectra. In the copolymerizations of DPE (M_2) with styrene (M_1) and dienes (M_1),[1-4] the M_1 monomers were completely consumed in a prolonged reaction. In the present work, however, both o- and p-MeOSt were not completely incorporated into the copolymers in THF even after a prolonged time. A probable reason for this may be equilibrium copolymerization of the combinations of DPE and MeOSt.

The monomer reactivity ratios, r_1, determined in the copolymerizations of DPE (M_2) and several comonomers (M_1) by means of n-BuLi are collected in Table V. It is interesting that the relative reactivities of o-MeOSt and DPE in THF and in benzene were reversed, but that no inversion was observed in the pairs, DPE-p-MeOSt and DPE-styrene, in these solvents. In hydrocarbon solvents, o-MeOSt may coordinate with the lithium counter-ion at the polymer end in such a way

that the end easily attacks the vinyl group of the monomer, while such an arrangement will probably be difficult for p-MeOSt. These may be correlated with the fact that o-MeOSt gave an isotactic polymer in toluene with n-BuLi,[6] and p-MeOSt gave an atactic one.[10] The coordination seems to be stronger at low temperatue, which will result in higher relative reactivity of o-MeOSt, and to be weaker with Na^+ (Table III). The addition of THF, a stronger base, to the system prevents the coordination of o-MeOSt. Therefore, the relative reactivity of the o-MeOSt in THF should be low as is shown in Table III. Similar results were also obtained in the copolymerizations of DPE with butadiene and isoprene (Table V). Korotkov *et al.* have explained the higher reactivities of butadiene[11] and isoprene[12] in hydrocarbon solvents by the preferential absorptions of the dienes to reaction centers.

Table V. Monomer reactivity ratio, r_1, in the copolymerizations of DPE (M_2) with other comonomers (M_1) by n-BuLi

M_1	THF[a]	Benzene[b]	Ref.
Styrene	0.13	0.44[c]	1
p-MeOSt	~0	<0.3	This work
o-MeOSt	~0	20	This work
Butadiene	0.13	54	15
Isoprene	0.11	37	3
2,3-Dimethyl-butadiene	0[d]	0.23	2,4

[a] At 0°C, [b] At 40°C, [c] In toluene at 30°C, [d] At 22°C.

Recently, Worsfold *et al.*[13,14] found that the rates of the additions of styrene to butadienyl-lithium and isoprenyllithium are nearly constant whether the dienes exist in the systems or not, and denied the preferential absorptions of the dienes to lithium counter-ion in the copolymerizations of styrene with the dienes. Anyhow, though it is clear that there are some differences in the reaction mechanisms in hydrocarbon and THF with lithium catalyst, the nature of such differences is not yet clearly understood.

The NMR spectrum of the alternating copolymer of *o*-MeOSt and DPE shows three peaks due to the methoxy group (Figure 2). Since there is no such configurational isomer in the three units, DPE-*o*-MeOSt-DPE, at least five units must be considered for this methoxy splitting.
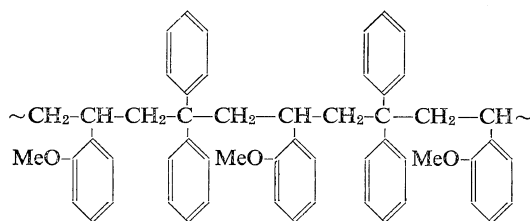
If the DPE units are ignored in the above sequence, the configurations of three *o*-MeOSt units may be treated as the triad sequence of the *o*-MeOSt homopolymer. Then, three different configurations in the above five monomer units are possible, which may have corresponding resonance peaks in the NMR spectrum as is shown in Figure 2. It has been found that in the NMR spectrum of the P-*o*-MeOSt the methoxy resonance was split into ten peaks by the pentad sequence.[6] These results show that the resonances of the *o*-methoxy groups in both the homopolymer and copolymer are very sensitive to the configurational difference

in the polymers. The methoxy resonance of the alternating copolymer of *p*-MeOSt and DPE was not so clearly split (Figure 3). However, the stereoregularity of this copolymer seems to be rather different from that of the alternating copolymer of DPE and *o*-MeOSt; this may affect the crystallinities of the copolymers.

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