Polymerization of an Azastyrene Derivative. 2. Copolymerization of 2,6-Diisopropyl-*N*-methylenaniline with Maleic Anhydride[†]

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Introduction

Although a number of compounds containing C═C or C═O double bonds have been polymerized to high molecular weight polymers by radical or ionic initiators, there are no papers on the addition polymerization of compounds with C═N double bonds, to our knowledge, except for carbodiimide,[1, 2] isocyanates,[3−5] imines,[6] 1-azabutadiene,[6] and azine compounds.[7−16] Although 2,3-diaza-1,3-butadiene, formaldehyde azine (CH_2═N−N═CH_2), which is the simplest azine, was prepared in 1959,[7] there had been no systematic studies concerning the polymerization of the azine compound before the study by Kamachi *et al.*[8,9] We have systematically investigated polymerizabilities of other azine compounds to understand polymerizabilities of the C═N double bond and to obtain new polymers.[10−12] As a result, we have succeeded in the formation of *trans*-1,4-polymer from alkyl azine compounds (RCH═N−N═CHR, R = CH_3, C_2H_5, *n*-C_3H_7)[13−15] and in that of 1,2-polymer from trifluoroacetaldehyde azine (R = CF_3).[16]

Recently, in the expansion of this research, we have also paid attention to *N*-methylenaniline (CH_2═NC_6H_5). Since *N*-methylenaniline is a styrene analogue containing a C═N double bond, the polymerization of this compound has long been examined.[17] Although *N*-methylenaniline is known to be stable in the gas phase,[18] it has been reported that *N*-methylenaniline is too unstable to be isolated in its condensed phase because it is immediately converted to a cyclic trimer, hexahydro-1,3,5-triphenyl-1,3,5-triazine.[19]

In 1985, Verardo *et al.* reported a stable monomeric azastyrene derivative, 2,6-diisopropyl-*N*-methylenaniline (DiPMAn), whose isopropyl groups retarded the cyclic trimerization.[20,21] To our knowledge, however, no paper had been reported on the polymerizability of DiPMAn. Therefore, we investigated the polymerizability of DiPMAn and found that DiPMAn was polymerized by cationic initiators, such as trifluoroacetic acid (TFA), $TiCl_4$−TFA, and $SnCl_4$−TFA, to form 1,6-addition polymer.[22]

When DiPMAn was added to maleic anhydride (MAnh), spontaneous polymerization took place to form a resin. Therefore, we investigated the copolymerization of DiPMAn and MAnh and found that the copolymer was formed by alternating copolymerization. In this paper, we will describe the formation of the copolymer and its structure.

Experimental Section

DiPMAn was prepared from 2,6-diisopropylaniline and paraformaldehyde according to the method of Verardo *et al.*[20] DiPMAn was purified by successive distillations under reduced pressure over calcium hydride and stored under an argon atmosphere. The purity of DiPMAn was checked by gas chromatography (GC) and 270 MHz ^{1}H NMR spectroscopy.

MAnh was recrystallized in chloroform. Tetrahydrofuran (THF), 1,4-dioxane, and toluene were purified by distillation over sodium benzophenone ketyl under an argon atmosphere.

A typical copolymerization of DiPMAn with MAnh is described below. MAnh (98 mg, 1.0 mmol) and 1,4-dioxane (0.5 mL) were placed in an ampule under an argon atmosphere. When DiPMAn (0.19 mL, 1.0 mmol) was added to the solution of MAnh in 1,4-dioxane, the reaction mixture changed from colorless to pale yellow. Then the ampule was sealed under an argon atmosphere. The sealed ampule was immersed in the oil-bath whose temperature was maintained at 80 °C. After 24 h, the ampule was opened and hexane (5 mL) was poured into the ampule to form precipitate. The precipitate was separated from the solution by centrifugation. Copolymer was obtained as colorless powder by reprecipitation in THF−hexane (1:10).[23]

In the continuous variation method, the total amounts of DiPMAn and MAnh were fixed at 2.0 mmol, while the molar fractions of DiPMAn were varied from 0 to 1.0. A given amount of MAnh and 1,4-dioxane (0.5 mL) was placed in an ampule under an argon atmosphere. Then a given amount of DiPMAn was added to the solution of MAnh in 1,4-dioxane. Afterward the ampule was sealed under an argon atmosphere. The sealed ampule was immersed in an oil bath whose temperature was maintained at 80 °C. After 24 h, the ampule was opened and hexane (5 mL) was poured into the ampule to form precipitate. The precipitate was separated from the solution by centrifugation. Copolymer was obtained as colorless powder by reprecipitation in THF−hexane (1:10). The molar fractions of DiPMAn in copolymer were determined by elemental analysis.

Gel permeation chromatography (GPC) analyses were performed in THF with a TOSOH CCP & 8010 system by using TSK gel at 40 °C. TOSOH UV-8010 and TOSOH RI-8012 detectors were used. The molecular weights were calibrated by standard polystyrene. Vapor pressure osmometry (VPO) measurements were carried out on a Knauer Vapor Pressure Osmometer No. A0280 by using toluene as a solvent at 60 °C. The molecular weights were calibrated by benzil (C_6H_5-$COCOC_6H_5$). IR spectra were recorded on a JASCO FT/IR-3 spectrometer. ^{1}H NMR spectra were observed on a JEOL JNM-EX270 using $CDCl_3$ as a solvent at 30 °C. Mass spectra were recorded on a JEOL JMS SX-102 mass spectrometer by the electron impact (EI) method. Mass number was calibrated by using cesium iodide (CsI). GC analyses were performed on a Shimadzu GC-8A gas chromatograph with a silicone (DC550, Gasukuro Kogyo Inc.) column.

Results and Discussion

Results on the copolymerization of DiPMAn with MAnh are shown in Table 1. In each case, copolymer was obtained in a high yield (70−90%). The copolymer whose molecular weight was as high as 10 000 was obtained under a neat condition. The number-average molecular weights estimated by VPO were nearly equal to those determined by GPC. A higher yield of the copolymer was obtained in 1,4-dioxane than in toluene.

In order to get information on what type of copolymerization occurred, the continuous variation method was carried out. The result is shown in Figure 1. The maximum of the yield of the copolymer is observed at the mole fraction of DiPMAn of 0.5. Figure 2 shows the dependence of the mole fraction of DiPMAn in copolymer on the composition of DiPMAn in the feed. It shows that the mole fractions of DiPMAn in copolymer are almost the same (∼0.5), being independent of the composition of the charged comonomer. These results suggest that the obtained copolymers were formed by alternating copolymerization.

[†] For part 1 in this series, see ref 22.

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Table 1. Copolymerizations of DiPMAn with MAnh

DiPMAn, mmol	MAnh, mmol	solvent (M)	temp, °C	time, h	yield, %	$10^3 \bar{M}_w$,[a]	$\bar{M}_w/\bar{M}_n$[a]
10.0[b]	10.0		80	8	72.5	9.7	1.26
1.0[c]	1.0		80	24	86.1	6.9	1.20
1.0[c]	1.0	toluene (4.0)	80	24	78.7	5.7	1.21
1.0[c]	1.0	1,4-dioxane (4.0)	80	24	89.5	7.8	1.19
10.6[c]	10.6	THF (4.0)	25	60	84.5	7.6	1.33

[a] Determined by GPC, calibrated by standard polystyrene. [b] Under high vacuum. [c] Under an argon atmosphere.

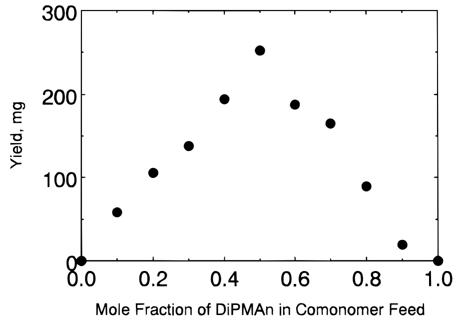


Figure 1. Continuous variation plots for the copolymerization of DiPMAn and MAnh in 1,4-dioxane under an argon atmosphere at 80 °C. Total amounts of DiPMAn and MAnh were fixed at 2.0 mmol.

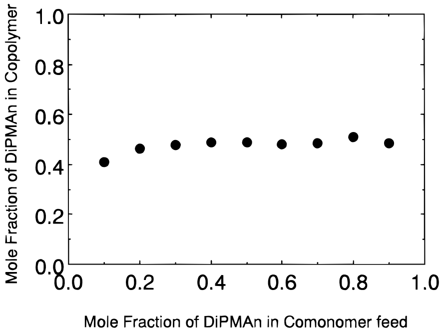


Figure 2. Dependence of the mole fraction of DiPMAn in the obtained copolymer on the mole fraction of DiPMAn in the comonomers feed.

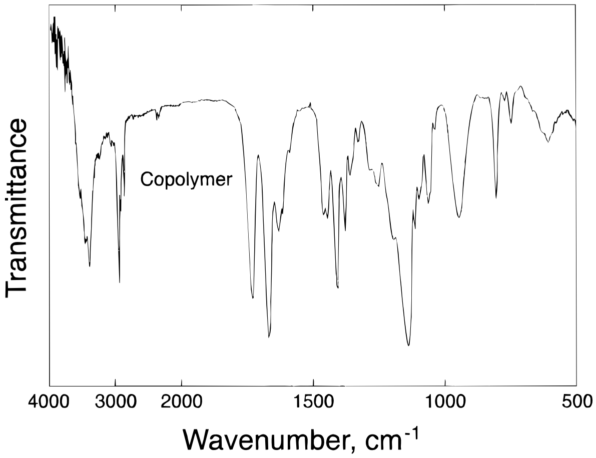


Figure 3. IR spectrum of the obtained copolymer (KBr).

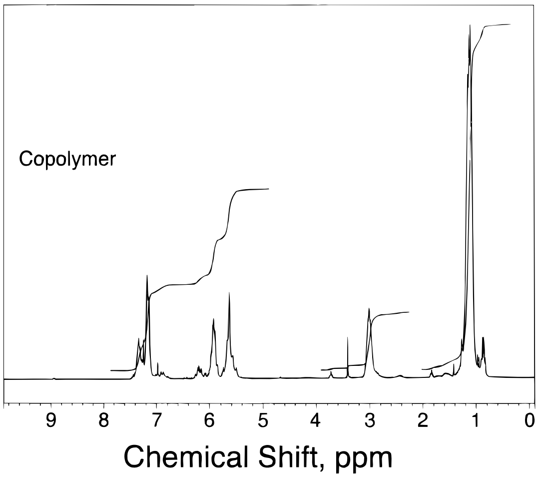


Figure 4. 270 MHz ^{1}H NMR spectrum of the obtained copolymer ($CDCl_3$).

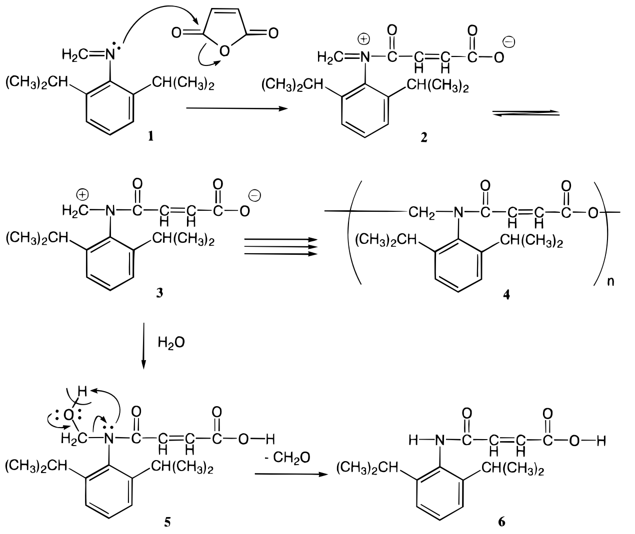
The structure of the obtained copolymer was investigated by IR and ^{1}H NMR spectroscopies. The IR spectra of DiPMAn and the copolymer are shown in Figure 3. In the spectrum of the copolymer, the absorption bands assignable to the stretching vibration of the C=O double bonds of the ester and amide groups are observed at about 1740 and 1670 cm^{-1}, respectively.[24] The absorption band observed at about 1630 cm^{-1} in the spectrum of the copolymer is due to the stretching vibration of the aromatic C=C double bond.[25] Furthermore, the absorption bands due to the symmetric and the antisymmetric stretching vibrations of the C–O–C bonds of the ester group are observed at about 950 and 1160 cm^{-1} in the spectrum of the copolymer, respectively.[24] These results suggest that esterification and amidation took place during the copolymerization. In addition, in the IR spectrum of the copolymer, the absorption band assignable to the stretching vibration of the O–H bond is observed at about 3400 cm^{-1}.[24] The 270 MHz ^{1}H NMR spectra of DiPMAn and the obtained copolymer are shown in Figure 4. The absorption bands due to the olefinic protons are observed at about 5.8–6.2 ppm.[26] This result suggests that the C=C double bond derived from MAnh remain after copolymerization.

On the basis of these results, we can deduce that the obtained copolymer is composed of the structure (**4**) shown in Scheme 1. The absorption band, observed at about 3400 cm^{-1} in the IR spectrum of the copolymer, can be ascribed to the carboxyl group of the chain end.

A proposed mechanism for the copolymerization of DiPMAn with MAnh is shown in Scheme 1. Since the carbonyl carbon should be the most electron-poor atom in MAnh, the lone pair of the nitrogen of DiPMAn attacks the carbonyl carbon of MAnh rather than the vinyl group to form a zwitterion (steps **1** to **3**). The alternating copolymer of DiPMAn with MAnh is produced by the coupling reactions between the zwitterions (steps **3** to **4**). Similarly, Saegusa *et al.* have reported the alternating copolymerizations between *N*-benzilideneanililne and succinic anhydride via zwitterion mechanism.[27]

In the course of the purification of the copolymer, colorless crystals were obtained from the copolymerization system. The chemical structure of the crystalline product was investigated by elemental analysis, EI-mass, IR, and ^{1}H NMR spectroscopies.[28] From these results, we can conclude that the product is composed of the structure (**6**) shown in Scheme 1. The product is considered to be formed by the reaction of zwitterion

Scheme 1. Proposed Mechanism of the Copolymerization of DiPMAn with MAnh



(**3**) with water, which is contained in the precipitant. This mechanism was confirmed by the fact the yield of the product increased upon the addition of water to the polymerization system in the process of the copolymerization. These results also support the zwitterion mechanism.

From these results, we can conclude that the copolymerization proceeds via the zwitterion (**3**) and that the copolymer has the structure (**4**).

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(23) Copolymer: yield 257 mg, 89.5%; mp, 160−165 °C; IR (KBr), 1730 (s; ester C=O), 1670 (vs; amide C=O), 1155 (s; ester C−O−C), 950 (m; ester C−O−C), 810 (m; out-of-plane C−H), 750 (m; out-of-plane C−H) cm^{-1}; ^{1}H NMR (CDCl$_3$): δ = 1.0−1.4 (6H, CH$_3$), 2.9−3.1 (2H, CH), 5.5−5.8 (2H, COOCH$_2$NCO), 5.8−6.3 (2H, CH=CH), 7.1−7.5 (3H, phenyl). Anal. Calcd for $(C_{17}H_{21}NO_3)_n$: C, 71.06; H, 7.37; N, 4.87. Found: C, 70.46; H, 7.51; N, 4.59.
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(28) Colorless crystals: yield, 49 mg, 1.8%; mp, 183−184 °C; IR (KBr), 3400 (OH), 3200 (NH), 1700 (s; C=O), 1630 (vs; aromatic C=C), 790 (m; out-of-plane C−H), 740 (m; out-of-plane C−H) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ = 1.2 (d, 6H, CH$_3$), 3.0 (m, 2H, CH), 6.4 (d, 1H, CH=), 6.7 (d, 1H, CH=), 7.2−7.4 (m, 3H, phenyl), 8.5 (s, 1H, NH), 15.8 (s, 1H, COOH). Anal. Calcd for $C_{16}H_{21}NO_3$: C, 69.79; H, 7.69; N, 5.09. Found: C, 69.72; H, 7.68; N, 5.06. EI-MS [M^{+}] calcd 275, found 275.

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