BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 3207—3210 (1969)

The Polymerizations and Copolymerizations of α-Methoxyacrylonitrile and Methyl α-Methoxyacrylate

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(Received December 12, 1968)

A study of the polymerizations and copolymerizations of α-methoxyacrylonitrile(MeOAN) and methyl α-methoxyacrylate(MeOA) has been made. These monomers were homopolymerized with a radical initiator at 60°C, but did not give any polymer with such ionic catalysts as $BF_3O(C_2H_5)_2$ and C_6H_5MgBr at 0°C. From the radical copolymerizasions of these monomers with styrene at 60°C, their Q and e values were determined to be as follows:

$$Q = 0.72,\ e = 0.40 \quad \text{for MeOAN}$$

$$Q = 0.47,\ e = 0.04 \quad \text{for MeOA}$$

These monomers were also copolymerized with acrylonitrile, and the copolymerization parameters were determined.

In previous papers, it was pointed out that some α-substituted acrylate monomers, such as methyl α-cyanoacrylate[1] and alkyl α-phenylacrylate,[2] showed remarkably higher copolymerization reactivities than the respective unsubstituted monomers, such as methyl acrylate, acrylonitrile, and styrene. Similar enhanced reactivities of the monomers upon the introduction of some α-substituents have also been observed in the reported copolymerization data.[3]

By using these copolymerization data, we recently found that α-substituents of acrylonitrile and acrylic esters contributed additively to the values of e and $\log Q$ in the following equations, (1) and (2):[4]

$$\begin{aligned} e_{\mathrm{CH_2=C}\langle^{\mathrm{X}}_{\mathrm{Y}}} &= e_{\mathrm{CH_2=C}\langle^{\mathrm{H}}_{\mathrm{Y}}} + 2.4\sigma_{\mathrm{X}} \\ &= e_{\mathrm{CH_2=C}\langle^{\mathrm{X}}_{\mathrm{H}}} + 2.4\sigma_{\mathrm{Y}} \qquad (1) \\ \log Q_{\mathrm{CH_2=C}\langle^{\mathrm{X}}_{\mathrm{Y}}} &= \log Q_{\mathrm{CH_2=C}\langle^{\mathrm{H}}_{\mathrm{Y}}} + (\log Q_{\mathrm{CH_2=C}\langle^{\mathrm{X}}_{\mathrm{H}}} - \log Q_{\mathrm{CH_2=CH_2}}) \\ &= \log Q_{\mathrm{CH_2=C}\langle^{\mathrm{H}}_{\mathrm{Y}}} + \Delta\log Q_{\mathrm{X}} \end{aligned}$$

or

$$\begin{aligned} \log Q_{\mathrm{CH_2=C}\langle^{\mathrm{X}}_{\mathrm{Y}}} &= \log Q_{\mathrm{CH_2=C}\langle^{\mathrm{X}}_{\mathrm{H}}} + (\log Q_{\mathrm{CH_2=C}\langle^{\mathrm{H}}_{\mathrm{Y}}} - \log Q_{\mathrm{CH_2=CH_2}}) \\ &= \log Q_{\mathrm{CH_2=C}\langle^{\mathrm{X}}_{\mathrm{H}}} + \Delta\log Q_{\mathrm{Y}} \qquad (2) \end{aligned}$$

where X represents the methoxy, methyl, hydrogen, chloro, bromo, acetoxy, carboalkoxy, and cyano groups, and Y cyano and carboalkoxy groups.

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[1] T. Otsu and B. Yamada, *Makromol. Chem.*, **110**, 297 (1967).

[2] T. Otsu, B. Yamada and T. Nozaki, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **70**, 1941 (1967).

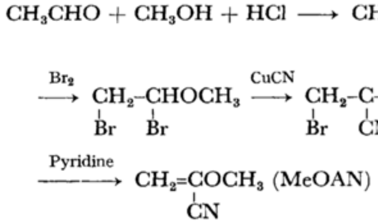
[3] H. Mark, B. Immergut, E. H. Immergut and L.J. Young, "Copolymerization," ed. by G. E. Ham, Interscience (1964), p. 695.

[4] B. Yamada and T. Otsu, *J. Macromol. Sci.-Chem.*, ***A3***, 1551 (1969).

In the course of studying the effect of the α-substituents of vinyl monomers on their radical reactivities, α-methoxy acrylonitrile (MeOAN) and methyl α-methoxyacrylate (MeOA) were prepared and copolymerized with styrene and acrylonitrile. The present paper will describe the results thus obtained. Since it has been generally known that some 1,1-disubstituted ethylenic monomers, especially α-substituted styrenes, have low ceiling temperatures,[5] the homopolymerizabilities of these monomers will also be described in this study.

Experimental

Preparations of Monomers. The MeOAN monomer was prepared by the method described by Baker[6] through the following reaction path:



$$CH_3CHO + CH_3OH + HCl \longrightarrow \underset{\displaystyle Cl}{CH_2}CHOCH_3$$

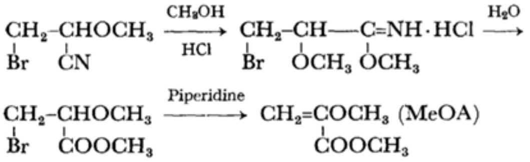
$$\xrightarrow{Br_2} \underset{\displaystyle Br}{CH_2}-\underset{\displaystyle Br}{CH}OCH_3 \xrightarrow{CuCN} \underset{\displaystyle Br}{CH_2}-\underset{\displaystyle CN}{C}-OCH_3$$

$$\xrightarrow{\text{Pyridine}} CH_2{=}\underset{\displaystyle CN}{C}OCH_3 \text{ (MeOAN)}$$

The resulting MeOAN monomer was purified by fractional distillations under reduced pressure: bp 32—33°C/22 mmHg. (lit,[6] 32.5°C/23 mmHg), n_D^{20} 1.4155, d_4^{15} 0.942.

Found: C, 58.23; H, 6.13%. Calcd for C_4H_5NO: C, 57.83; H, 6.07%.

The MeOA monomer was also obtained as follows:



$$\underset{\displaystyle Br}{CH_2}-\underset{\displaystyle CN}{CH}OCH_3 \xrightarrow[HCl]{CH_3OH} \underset{\displaystyle Br}{CH_2}-\underset{\displaystyle OCH_3}{CH}-\underset{\displaystyle OCH_3}{C}{=}NH\cdot HCl \xrightarrow{H_2O}$$

$$\underset{\displaystyle Br}{CH_2}-\underset{\displaystyle COOCH_3}{CH}OCH_3 \xrightarrow{\text{Piperidine}} CH_2{=}\underset{\displaystyle COOCH_3}{C}OCH_3 \text{ (MeOA)}$$

The resulting MeOA monomer was also purified by fractional distillation: bp 52.5—53.0°C/11 mmHg. (lit,[6] 51.5—52.0°C/11 mmHg), n_D^{20} 1.4347 (lit,[6] 1.4316), d_4^{15} 1.068.

Found: C, 51.65; H, 6.98%. Calcd for $C_5H_8O_3$: C, 51.72; H, 6.90%.

Other Reagents. The styrene and acrylonitrile were purified by ordinary methods and were distilled under reduced pressure before use. The α,α'-azobis-isobutyronitrile(AIBN) was recrystallized from ethanol. The benzene, methylene chloride, and toluene were used after purification by ordinary methods.

Radical Polymerizations and Copolymerizations. The required amounts of the monomer, AIBN, and the solvent were charged into a polymerization ampoule. After it had then been degassed by a freezing and thawing method, the ampoule was sealed off under a vacuum.

The polymerizations and copolymerizations were carried out at 60°C under shaking. After polymerization for a given time, the content of the ampoule was poured into a large amount of mehanol (the homopolymer of MeOAN and copolymers) or diethyl ether (the homopolymer of MeOA) to precipitate the polymer. The resulting copolymers with styrene and with acrylonitrile were purified by the reprecipitation method from benzene-methanol and dimethylformamide-methanol systems respectively.

The compositions of the copolymers were calculated from their carbon or nitrogen content, and the monomer reactivity ratios were determined by the Fineman-Ross[7] and curve-fitting methods.

Ionic Polymerizations. The cationic polymerizations of these monomers were carried out by the use of boron trifluoride diethyl etherate in methylene chloride at 0°C. The anionic polymerizations were performed with phenylmagnesium bromide in toluene at 0°C. After a given polymerization time, the reaction mixture was poured into a large excess of methanol or diethyl ether.

Results and Discussion

Homopolymerizations of MeOAN and MeOA. The results of the homopolymerizations of MeOAN and MeOA monomers with radical and ionic initiators are shown in Table 1.

From Table 1, it can be seen that these monomers were homopolymerized only by the AIBN initiator

TABLE 1. HOMOPOLYMERIZATIONS OF MeOAN AND MeOA MONOMERS

Monomer (ml)		Initiator (g)	Solvent (ml)	Temp. (°C)	Time (hr)	Yield (%)
MeOAN	0.6	AIBN, 0.0023	C_6H_6, 1.0	60	150	8.9
	0.5	$BF_3O(C_2H_5)_2$, 0.009	CH_3Cl_2, 0.5	0	24	0
	1.0	C_6H_5MgBr*	$C_6H_5CH_3$, 1.0	0	24	0
MeOA	1.0	AIBN, 0.0022	C_6H_6, 1.5	60	150	25.7**
	0.5	$BF_3O(C_2H_5)_2$, 0.009	CH_2Cl_2, 0.5	0	24	0
	1.0	C_6H_5MgBr*	$C_6H_5CH_3$, 1.0	0	24	0

* Used 1 ml of its tetrahydrofuran solution prepared from 13.5 g of bromobenzene and 2 g of magnesium in 55 ml of tetrahydrofuran.

** Specific viscosity (η_{sp}/c) of this polymer was 0.197 (c=1.05 g/100 ml benzene).

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[5] H. Lüssi, *Chimia*, **20**, 379 (1966).

[6] J. W. Baker, *J. Chem. Soc.*, **1942**, 520.

[7] M. Finneman and S. D. Ross, *J. Polymer Sci.*, **5**, 269 (1950).

TABLE 2. COPOLYMERIZATIONS OF MeOAN AND MeOA (M_1) WITH STYRENE (M_2) AT 60°C

($[M_1]+[M_2]$) = 8 mol/l in benzene.*

M_1	$[M_1]$ in comonomer (mol%)	Time (hr)	Conversion (%)	Copolymer obtained N (%)	C (%)	$[M_1]$ (mol%)
MeOAN	16.0	10.2	8.3	3.04	—	21.6
	30.0	10.5	4.1	4.90	—	33.9
	43.1	27.2	10.2	6.22	—	42.3
	53.4	28.0	8.1	7.12	—	47.8
	63.2	53.0	10.0	8.39	—	55.5
	75.4	53.5	8.0	9.55	—	61.5
	83.9	61.5	6.0	11.36	—	72.3
MeOA	13.6	4.0	6.8	—	86.81	12.0
	26.1	5.5	7.9	—	82.80	21.5
	37.9	5.5	7.1	—	78.24	32.2
	49.7	6.5	7.1	—	74.33	41.6
	61.3	6.25	6.3	—	70.70	50.5
	75.0	8.0	5.3	—	64.80	65.3
	84.1	9.33	6.4	—	60.53	76.4

* In the copolymericaztions of MeOAN and MeOA, the concentrations of AIBN were kept constant at 4.63×10^{-3} and 5.06×10^{-3} mol/l, respectively.

under the present conditions. However, their rates were quite low compared with those of the respective unsubstituted monomers, acrylonitrile and methyl acrylate. Between the two monomers, the homopolymerizability of MeOA was larger than that of MeOAN. This tendency was identical to that observed in the radical homopolymerizabilities for α-methyl substituted monomers, such as methacrylonitrile and methyl methacrylate. It was also obvious that these monomers have ceiling temperatures higher than 60°C.

Although these monomers have both an electron-donating methoxy substituent and an electron-withdrawing cyano or carbomethoxy substituent, they were not found to give any homopolymer with cationic and anionic catalysts ($BF_3O(C_2H_5)_2$ and C_6H_5MgBr respectively) at 0°C.

Copolymerizations of MeOAN and MeOA with Styrene. Table 2 shows the results of the radical copolymerizations of MeOAN and MeOA (M_1) with styrene (M_2) at 60°C.

From Table 2, the rate of copolymerization was found to decrease with an increase in the concentration of MeOAN or MeOA in the feed-monomer mixture. The monomer-copolymer composition curves are shown in Fig. 1.

The copolymerization parameters (r_1, r_2, Q_1 and e_1) were determined to be as follows:

for MeOAN (M_1)-styrene (M_2):

$$r_1 = 0.35,\ r_2 = 0.53,\ Q_1 = 0.72,\ e_1 = 0.40$$

for MeOA (M_1)-styrene (M_2):

$$r_1 = 0.51,\ r_2 = 1.10,\ Q_1 = 0.47,\ e_1 = 0.04$$

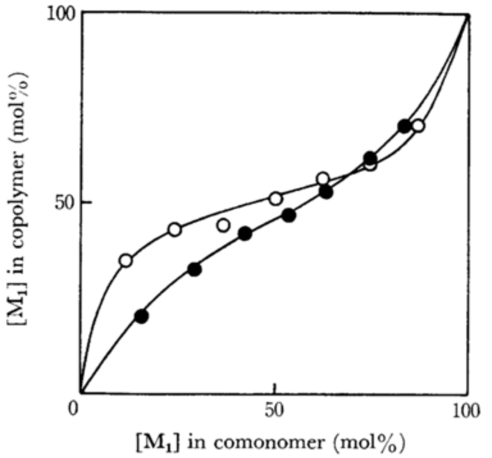

Fig. 1. Monomer-copolymer composition curves for MeOAN (M_1)-styrene(M_2) (○) and MeOA(M_1)-styrene(M_2) (●) at 60°.

where the Q_1 and e_1 values were calculated by assuming that the Q_2 and e_2 values were 1.0 and −0.80 respectively.

The values of e_1 and Q_1 obtained for MeOAN and MeOA were then compared with those calculated from Eqs. (1) and (2). When the values of e and log Q for acrylonitrile and methyl acrylate used were $e=1.20$ and log $Q=-0.22$, and $e=0.60$ and log $Q=-0.38$ from the literature,[3] and when those of Δ log Q and σ for the methoxy substituent used were 0.06 and −0.27, as reported in a previous paper,[4] the following values of Q_1 and e_1 were obtained:

for MeONA: $Q_1 = 0.69$, $e_1 = 0.49$

for MeOA: $Q_1 = 0.48$, $e_1 = -0.11$

It was clear that the Q_1 and e_1 values calculated from Eqs. (1) and (2) were in agreement with those obtained in this experiment; the validity of the above equations was thus confirmed.

Copolymerizations of MeOAN and MeOA with Acrylonitrile. The results of the radical copolymerizations of these monomers (M_1) with acrylonitrile (M_2) are shown in Table 3, while the resulting copolymer composition curves are indicated in Fig. 2.

The following copolymerization parameters were obtained:

for MeOAN (M_1)-acrylonitrile (M_2):

$$r_1 = 1.93,\ r_2 = 0.37,\ Q_1 = 0.83,\ e_1 = 0.61$$

for MeOA (M_1)-acrylonitrile (M_2):

$$r_1 = 0.30,\ r_2 = 0.15,\ Q_1 = 0.48,\ e_1 = -0.56$$

where the Q_1 and e_1 values were calculated by assuming that $e_2 = 1.20$ and $Q_2 = 0.60$ for acrylonitrile.

Contrary to the results of the copolymerizations with styrene, the relative reactivities ($1/r_2$) of these monomers toward a polyacrylonitrile radical were

TABLE 3. COPOLYMERIZATIONS OF MeOAN AND MeOA (M_1) WITH ACRYLONITRILE (M_2) AT 60°C

($[M_1]+[M_2]$) = 8.00 mol/l in benzene*

M_1	$[M_1]$ in comonomer (mol%)	Time (hr)	Conversion (%)	Copolymers obtained	
				N (%)	$[M_1]$ (mol%)
MeOAN	12.0	5.6	17.3	23.01	25.4
	25.0	31	8.4	21.00	43.9
	37.0	31	5.7	19.81	57.0
	50.0	31	3.5	18.84	68.5
	63.0	70	6.8	18.27	75.9
	75.0	106	6.7	17.50	86.2
	87.0	134	5.8	17.05	93.0
MeOA	12.0	5	12.9	11.81	36.1
	25.0	5	15.0	10.08	42.6
	37.0	5	15.1	8.83	44.3
	50.0	5	13.7	7.75	52.4
	63.0	5	11.6	6.39	58.9
	75.0	5	8.8	5.53	63.3
	87.0	5	5.4	3.83	72.9

* In the copolymerizations of MeOAN and MeOA, the concentrations of AIBN were kept constant at 5.47×10^{-3} and 5.00×10^{-3} mol/l, respectively.

found to be greater than those of the respective unsubstituted monomers of acrylonitrile and methyl acrylate, probably because of the electron-donating nature of the methoxy group. It was also noted that the e_1 value for MeOA obtained from the copolymerization with acrylonitrile was not in agreement with that obtained with styrene.

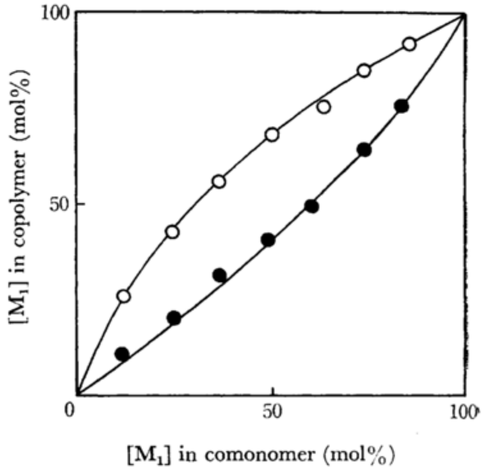

Fig. 2. Monomer-copolymer composition curves for MeOAN(M_1)-acrylonitrile(M_2) (○) and MeOA (M_1)-acrylonitrile(M_2) (●) at 60°C.

Although the Q and e values for α-substituted acrylonitriles and acrylic esters obtained from the copolymerizations with styrene were in agreement with those calculated from Eqs. (1) and (2), those obtained from the copolymerizations with acrylonitrile did not agree. In Table 4, the Q_1 and e_1 values of several α-substituted acrylonitriles and acrylic esters calculated from the copolymerizations with styrene and with acrylonitrile are summarized. In this table, the negative e_1 values of α-substituted acrylic esters carrying the electron-donating methyl and methoxy groups are noted; their e_1 values are not those with would be predicted from Eq. (1). However, no such abnormal behavior was found in the copolymerizations of α-substituted acrylonitriles, and Eqs. (1) and (2) were valid for the copolymerization with acrylonitrile.

The effects of electron-donating α-substituents on the relative reactivities of α-substituted vinyl monomers toward a polyacrylonitrile radical will be discussed in detail in a subsequent paper.

TABLE 4. THE VALUES OF Q_1 AND e_1 OF α-SUBSTITUTED ACRYLONITRILES AND α-SUBSTITUTED ACRYLIC ESTERS (M_1) DETERMINED FROM THE COPOLYMERIZATIONS WITH ACRYLONITRILE AND WITH STYRENE (M_2) AT 60°C

M_1	M_2: Acrylonitrile		M_2: Styrene		Ref.
	Q_1	e_1	Q_1	e_1	
α-Methoxyacrylonitrile	0.83	0.62	0.72	0.40	This work
Methacrylonitrile	1.45	0.63	1.12	0.81	3
α-Acetoxyacrylonitrile	1.18	1.10	1.17	1.06	8
Methyl α-methoxyacrylate	0.48	−0.56	0.47	0.04	This work
Methyl methacrylate	0.84	−0.12	0.74	0.40	3
Ethyl α-acetoxyacrylate	0.41	0.12	0.54	0.67	3, 4
Methyl acrylate	0.55	0.79	0.42	0.60	3

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8) T. Oota, M. Kobayashi and H. Ogawa, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **71**, 1542 (1968).