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Copolymerization of Cyclic Olefins, Trimethylethylene and Tetramethylethylene with Acrylonitrile*[1]

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The radical copolymerizations of cyclopentene, cyclohexene, cycloheptene, cyclooctene, trimethyl-, and tetramethyl-ethylene with acrylonitrile (AN, M_1) were carried out, and the reactivities of these monomers toward the AN radical ($1/r_1$) were found to be as follows: cyclopentene, 0.21; cyclohexene, 0.13; cycloheptene, 0.15; cyclooctene, 0.35; trimethylethylene, 0.37, and tetramethylethylene, 0.25. The reactivity of these internal olefins in radical polymerization was discussed.

In previous papers[1,2] dealing with the copolymerization of cyclic olefins and some methyl-substituted ethylenes with maleic anhydride, it was shown that the reactivity of the internal olefins toward the maleic anhydride radical seems to be mainly governed by the steric strain in the monomers. However, since both the comonomers of the copolymerization systems were internal olefins, the reference monomer, maleic anhydride, might have a steric influence on the reactivity. Acrylonitrile thus seemed to be more suitable as a reference monomer, for its use would eliminate this complexity. In this research, four cyclic olefins and two methyl-substituted ethylenes were copolymerized with acrylonitrile (AN) and the reactivities of these monomers toward the AN radical were compared with the reactivities toward the maleic anhydride radical.

The relative reactivities of cyclic olefins seem to be mainly governed by the ring strain of the olefins, and the lower reactivities of cyclohexene, cycloheptene, cyclooctene, and tetramethylethylene toward MAn are presumably due to the larger steric hindrance in the copolymerization with MAn than with AN. It was found that tri- and tetra-methylethylene showed a similar reactivity toward the AN radical, while tetramethylethylene was much less reactive toward the MAn radical.

Experimental

The monomers were purified as has been described previously[1,2] and were copolymerized in sealed ampoules at 60°C. Azobisisobutyronitrile (0.01 g) was used as an initiator for 2 g of the monomer mixture. The copolymers were formed as white precipitates in the system of cyclopentene, cycloheptene and trimethylethylene, and as yellow precipitates in the other systems. The copolymers were purified as has been shown previously.[3] The copolymer compositions were calculated from results of the nitrogen analysis as determined by the Kjeldahl method. The viscosity was measured in dimethylformamide, using an Ostwald viscometer at 30°C.

Results

The results of the copolymerization of cyclic olefins, trimethyl-, and tetramethyl-ethylene (M_2) with AN (M_1) are shown in Table 1. The rates of copolymerization (%/hr), and the viscosities of the copolymers of the cyclic olefins and AN are plotted against the monomer feed ratios in Fig. 1. The values for the trimethyl-, tetramethylethylene, and AN copolymers are shown in Fig. 2. The rates of polymerization decreased with an increase in the M_2 content of the monomer mixture. The order of rate was $C_5 > C_6 \gtrsim C_7 > C_8$. The order of the reactivity toward the AN radical was $C_8 > C_5 > C_7 > C_6$. Monomer reactivity ratios, as calculated by the Fineman-Ross method, are shown in Table 2. The negative values of r_2 should be taken to be zero, considering the experimental errors and the fact that practically none of the M_2 monomers homopolymerize.

Discussion

Reactivity of Cyclic Olefins. In Fig. 3, the relative reactivities of cyclic olefins toward the AN radical and the methyl radical[4] are shown,

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*[1] Paper XII in a series on "The Polymerization of Internal Olefins." For the preceding paper, see Ref. 3.

1) S. Murahashi, S. Nozakura and K. Yasufuku, This Bulletin, **38**, 2082 (1965).

2) S. Murahashi, S. Nozakura and K. Yasufuku, *ibid.*, **39**, 1338 (1966).

3) K. Yasufuku, S. Hirose, S. Nozakura and S. Murahashi, *ibid.*, **40**, 2139 (1967).

TABLE 1. COPOLYMERIZATION OF CYCLIC OLEFINS, TRIMETHYLETHYLENE AND TETRAMETHYLETHYLENE (M_2) WITH AN (M_1)

M_2	M_1 mmol	M_2 mmol	M_1 mol%	Polymn. time hr	Copolymer		
					Yield, %	N, %	m_1, mol%
Cyclopentene	28.1	6.6	80.98	0.4	4.4	24.89	95.58
	24.0	11.0	68.57	0.6	4.2	24.11	93.20
	32.3	23.7	57.68	0.7	2.3	22.95	89.61
	16.7	16.4	50.45	0.7	2.7	22.29	87.53
	9.5	19.2	33.11	9.8	9.4	21.03	83.48
	11.3	39.3	22.26	9.8	6.9	19.54	78.59
	7.4	63.0	10.47	10.0	1.8	17.69	72.34
Cyclohexene	24.8	5.7	81.31	1.1	12.4	25.36	97.50
	20.9	13.6	60.58	1.8	3.4	24.96	96.49
	14.7	18.4	44.41	2.4	3.2	24.77	96.01
	9.4	17.3	35.19	2.2	1.4	22.78	90.75
	5.2	21.9	19.16	6.6	1.3	21.57	87.42
Cycloheptene	22.7	9.2	71.16	2.1	4.8	24.13	95.13
	16.3	11.7	58.21	2.5	3.4	23.34	93.32
	10.6	14.0	43.08	4.5	2.8	22.41	91.13
	6.9	16.1	30.02	11.7	4.0	21.44	88.74
	5.0	17.2	22.54	26.4	4.4	20.51	86.37
Cyclooctene	23.8	6.9	77.52	1.2	1.2	22.44	92.22
	29.7	12.8	69.88	1.8	1.0	21.32	89.77
	28.2	12.7	68.94	3.2	1.8	20.73	88.42
	21.7	14.4	60.11	2.7	1.0	20.03	86.78
	15.9	13.7	53.73	8.6	4.0	20.97	88.96
	17.2	17.1	50.15	5.0	1.4	19.52	85.54
	13.1	20.3	39.21	8.8	1.2	18.65	83.37
	9.9	22.8	30.26	10.2	1.2	17.73	80.99
	7.1	31.3	18.50	49.1	3.7	16.55	77.78
Trimethylethylene	31.3	6.2	83.47	1.2	3.5	24.28	93.89
	24.1	13.3	64.91	1.9	1.5	22.23	87.64
	18.2	15.9	53.38	3.0	1.7	21.93	86.72
	10.9	22.1	33.02	7.0	1.3	20.79	83.11
	5.8	24.2	19.35	20.4	2.0	19.50	78.95
Tetramethylethylene	31.3	5.5	85.05	1.6	4.4	24.78	96.13
	27.1	8.7	75.70	2.1	2.1	23.80	93.64
	19.9	12.4	60.63	3.3	1.6	22.15	89.29
	17.1	14.9	53.45	2.2	2.0	21.72	88.10
	10.8	17.4	38.31	18.7	2.5	20.71	85.32

taking cyclohexene as a standard. The variation in the relative reactivities toward the AN radical with the number of carbon in cyclic olefin is similar to that in those of the methyl affinities ($C_8 > C_5 > C_7 > C_6$). The relative reactivities toward the MAn radical[1] are also reproduced in Fig. 3. In all three relative reactivities the minimum reactivity lies at cyclohexene and the patterns of the reactivity are different from that found in reaction through an ionic coordination process.[5]

In a paper concerning the reaction of diimide with cyclic and acyclic olefins,[6] Garbish *et al.* succeeded in calculating the theoretical relative ratios of the reaction rates. The calculated values were in good agreement with the observed values of the reaction rates. They considered the differences in the bond angles (ω) and torsional

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[4] J. Gresser, A. Rajbenbach and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 3005 (1961).

[5] K. Ziegler, H. Gellert, H. Martin, K. Nagel and J. Schneider, *Ann.*, **589**, 91 (1954); J. G. Traynham and M. F. Schnert, *J. Am. Chem. Soc.*, **78**, 4024 (1956); G. Dall'Asta and G. Mazzanti, *Makromolecular Chem.*, **61**, 178 (1963).

[6] E. W. Garbisch, Jr., S. M. Schildcrout, D. B. Patterson and C. M. Sprecher, *J. Am. Chem. Soc.*, **87**, 2932 (1965).

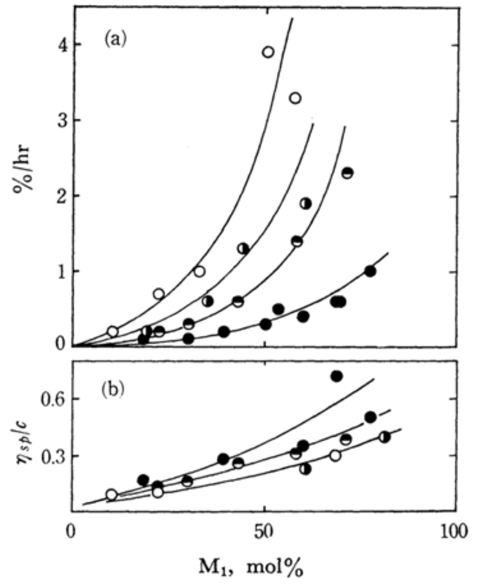


Fig. 1. Plot of overall copolymerization rate (%/hr) (a), and viscosity of copolymer (b) against monomer composition in the copolymerization of cyclic olefins (M_2) with AN (M_1): ○, cyclopentene; ◑, -hexene; ◐, -heptene; ●, -octene.

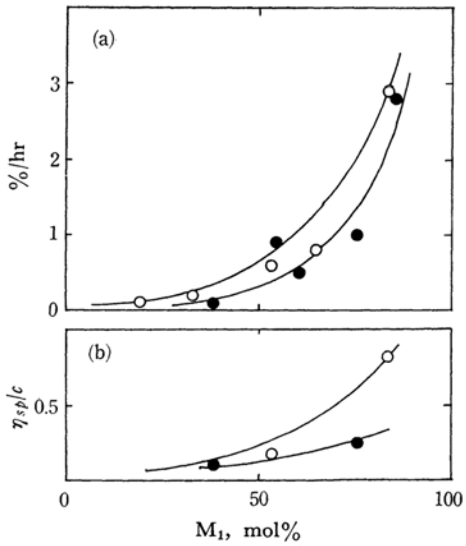
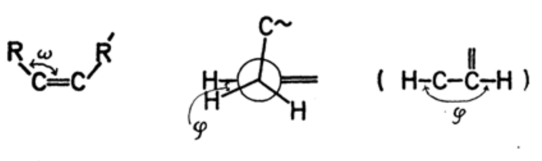


Fig. 2. The rate (a), and the viscosity (b) against the monomer composition in the copolymerization of trimethylethylene (○) and tetramethylethylene (●) (M_2) with AN (M_1).



angles (φ) of the olefins between the original and the transition state, which was assumed to be close to the original state. Garbish's theory is best applied to the reactivities of cyclic olefins. The theory suggests that the high reactivity of cyclopentene with diimide is attributable to the decrease in both the angle-bending strain and the torsional strain in the cyclopentene in the transition state. On the other hand, the torsional strain in cyclohexene increases in the transition state and the reactivity of cyclohexene is low. In cycloheptene and cyclooctene, the torsional strain again decreases in the transition state and the reactivity increases. Although the transition state for the radical-addition reaction may not be considered to be the same as that for the diimide reaction, both the transition states have been considered to be close to the original state.[7] Hence, it may be appropriate to consider that the variation in the radical reactivities of cyclic olefins with the number of the carbon in cyclic olefin is due to the change in the angle-bending strain and the torsional strain. The reactivity pattern of the cyclic olefins toward the MAn radical is different from that toward the AN radical and from the methyl affinity, as is shown in Fig. 3. A similarity in the reactivity patterns between the reactivities toward the AN radical attached to polymer chain and that toward the less bulky methyl radical suggests that the differences in the reactivity are mainly due to the ring strain of the cyclic olefins. The dissimilar reactivities toward the MAn radical are probably attributable to the

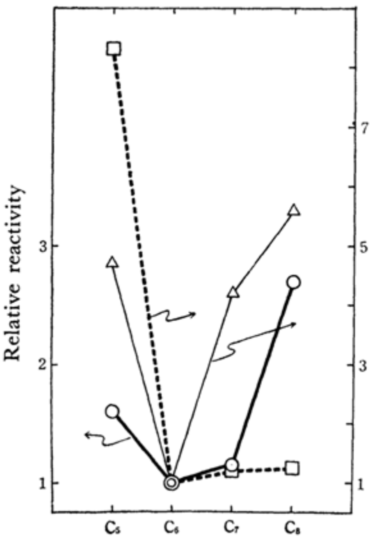


Fig. 3. Relative reactivities of cyclic olefins in the radical addition reactions; ○, in the copolymerization with AN; □, in the copolymerization with MAn; △, methyl affinity (Szwarc).

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[7] A. R. Bader, R. P. Buckley, F. Leavitt and M. Szwarc, *J. Am. Chem. Soc.*, **79**, 5621 (1957); M. Matsuoka and M. Szwarc, *ibid.*, **83**, 1260 (1961).

steric hindrance[8] of the cyclic olefins by the maleic anhydride ring.

Reactivity of Trimethylethylene and Tetramethylethylene. In the copolymerization with MAn, tetramethylethylene showed no reactivity. However, in the copolymerization with AN, it showed a reactivity comparable to that of trimethylethylene (Table 2). Szwarc reported that the reactivity of olefins with a methyl radical may be accounted for in terms of hyperconjugation. The much larger increase in the reactivity of the olefins accounted for in terms of hyperconjugation. The much larger increase in the reactivity of the olefins with the trifluoromethyl radical was concluded to arise from the electron-donating effect of a methyl group. The strongly electrophilic trifluoromethyl radical readily responds to such an effect. It was shown that the shielding effect of a CH_3 group on the rate of addition of the methyl radical is much less pronounced in trifluoromethyl addition.[9]

TABLE 2. MONOMER REACTIVITY RATIOS IN THE COPOLYMERIZATION OF CYCLIC OLEFINS, TRIMETHYL- AND TETRAMETHYLETHYLENE (M_2) WITH AN (M_1)

M_2	r_1	r_2	$1/r_1$
Cyclopentene	4.8 ± 0.36	-0.16 ± 0.34	0.21
Cyclohexene	8.0 ± 0.74	-0.42 ± 0.37	0.13
Cycloheptene	6.9 ± 0.35	-0.24 ± 0.12	0.15
Cyclooctene	2.8 ± 0.15	-0.28 ± 0.21	0.35
Trimethylethylene	2.7 ± 0.04	-0.27 ± 0.15	0.37
Tetramethylethylene	4.0 ± 0.03	-0.26 ± 0.04	0.25

In order to discuss the reactivity of methyl-substituted ethylenes, the data on their copolymerization with MAn and with AN are summarized in Table 3, along with our previous data[1,2] and those of other authors.[10,11] In Table 3 the trifluoromethyl radical affinities of these monomers[9] are also cited. Although the results on propylene have not been reported, they may be little different from those on butene-1.

TABLE 3. RELATIVE REACTIVITIES OF METHYL-SUBSTITUTED ETHYLENES IN THE VARIOUS COPOLYMERIZATION SYSTEMS

Ethylenes	MAn· %hr (at $M_1/M_2=1$)	AN· $1/r_1$	$CF_3\cdot$[8] k_2/k_1
$CH_2{=}CH{-}CH_2CH_3$	~2*	0.13**	687
$CH_2{=}C\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix}$	~120*	1.3**	1681
$\begin{smallmatrix}CH_3\diagdown\\ \end{smallmatrix}CH{=}CH\begin{smallmatrix}\diagup CH_3\\ \end{smallmatrix}$	~0.8	0.07**	580
$\begin{smallmatrix}\\ CH_3\diagup\end{smallmatrix}CH{=}CH\begin{smallmatrix}\diagup CH_3\\ \end{smallmatrix}$	~0.6	0.07**	585
$\begin{smallmatrix}\\ CH_3\diagup\end{smallmatrix}CH{=}C\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix}$	~10	0.37	—
$\begin{smallmatrix}CH_3\diagdown\\ CH_3\diagup\end{smallmatrix}C{=}C\begin{smallmatrix}\diagup CH_3\\ \diagdown CH_3\end{smallmatrix}$	~0	0.25	878

* Estimated values at $M_1/M_2=1$ from Ref. 9.
** Cited from Ref. 10.

Table 3 shows that the reactivities of methyl-substituted ethylenes are in the following orders:

Toward the AN radical ($1/r_1$):
isobutene > trimethylethylene > tetramethylethylene > butene-1 > butene-2
Toward the MAn radical (%/hr):
isobutene ≫ trimethylethylene > butene-1 > butene-2 > tetramethylethylene ≈ 0.

Since all the copolymerizations with MAn gave 1 : 1 alternating copolymers, the rates may be used to compare the reactivities. As Alfrey-Price's e values of MAn and AN are 2.25 and 1.20 respectively, both radicals are electron-attracting. The introduction of the electron-releasing methyl group into the monomer may result in the increase of its reactivity toward both the radicals. The introduction of a methyl group at the α-position increases the reactivity:

butene-1 → isobutene,
butene-2 → trimethylethylene.

This increase is due to the polar effect of the methyl substituent as well as to the resonance stabilizing effect on the resulting radicals. The introduction of a methyl group in the β-position decreases the reactivity:

isobutene → trimethylethylene,
butene-1 → butene-2

The decrease may be due to the steric effect of the β-methyl substituent.[3]

It is considered that the introduction of the fourth methyl group causes an increase in the steric hindrance at the β-position, resulting in a decrease in the reactivity; on the other hand, it results in an increase in the reactivity by increasing the polar factor. The fact that tetramethylethylene is rather reactive toward both the AN radical and the trifluoromethyl radical seems to show that the effect of the polar factor is considerable in both systems. On the other hand, tetramethylethylene does not copolymerize with the more electron-attracting MAn, in spite of the fact that the system showed a coloration due to the formation of a charge transfer complex. It is considered that the MAn copolymerization system is subject to a larger steric hindrance than is the AN copolymerization system. The copolymerization systems of internal olefins and MAn appear to have extreme features in that they give either alternating 1 : 1 copolymers or no polymer at all.

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[8] T. Alfrey, J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, N. Y. (1951), p. 51.

[9] A. P. Stefani, L. Herk and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 4732 (1961).

[10] T. Otsu, A. Shimizu and M. Imoto, *J. Polymer Sci.*, **B2**, 973 (1964).

[11] M. Imoto, A. Shimizu and T. Otsu, This Bulletin, **38**, 1535 (1965).