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INVESTIGATIONS OF THE MECHANISM OF ALTERNATING COPOLYMERIZATION WITH CHARGE-TRANSFER INTERACTION OF THE MONOMERS

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ABSTRACT

The applicability of the method of Giese to the measurement of the influence of monomer reactivity is examined. The reaction of alkyl mercuric salts with sodium borohydride permits the production of alkyl (cyclohexyl and butyl) radicals. Since hydrogen radicals are present in high concentration, the addition of alkenes to the reaction mixture leads to radicals from the alkenes. Further addition of alkene (polymerization) can be nearly completely excluded in this way. The composition of the reaction products is determined by gas chromatography. The addition rate of the alkenes relative to styrene allows correlation with the *e* value of the *Q*-*e* scheme of Alfrey and Price. The method answers the question of how far addition of the monomer complex occurs in one step or as separate addition of both monomers during copolymerization in the presence of charge-transfer (CT) complexes of the monomers. The investigations are performed by using the styrene/acrylonitrile/$ZnCl_2$ system, and it is demonstrated that the reactivity of the complexed

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*Dedicated to Dr Otto Vogl, Herman F. Mark Professor of Polymer Science at the Polytechnic University, Brooklyn, New York, on the occasion of his 60th birthday, November 6, 1987.

acrylonitrile is about 18 times greater than the one of the uncomplexed monomer. Investigation of mixtures of styrene with maleic anhydride and of isobutyl vinyl ether with maleic anhydride leads to proof that CT complexes are not highly reactive toward radicals compared to uncomplexed monomers. Furthermore, it can be shown that addition of the complex to the radical does not occur. These results lead to a degree of understanding of the mechanism of alternating copolymerization by CT interaction.

INTRODUCTION

The formation of alternating copolymers by radical polymerization has been known for many years. One of the monomers has marked electrophilicity; the other has to be an electron donor. Conjugated vinyl monomers, for instance, acrylates, often react with nucleophilic monomers to yield random copolymers, but it has been found [1] that such copolymers have completely alternating structures if they are prepared in the presence of a Lewis acid. Regardless of whether Lewis acids are present or not, there have been and there are still very different viewpoints concerning the mechanism of alternating copolymerization. They can be divided into two groups: 1) The addition of the monomer complexes from nucleophilic and electrophilic monomers in the propagation step [2-4] and 2) the separate addition of the monomers [5, 6, 9].

The characteristics of alternating copolymerization (e.g., maximum overall polymerization rate and molecular weight in the range of equimolar monomer concentration and formation of alternating copolymers over a wide range of monomer composition) have been interpreted in a large number of publications to result from addition of the monomer complex in the propagation step. Also, complex formation between the monomers has been conclusively demonstrated, but in most cases the complex concentration is rather low, so that the measured high polymerization rates can only be explained by assuming a very high reactivity of the CT complex.

The aim of this publication is to find out if the method of Giese [7, 8], which is generally very suitable for the measurement of reactivities, is capable of revealing changes in monomer reactivity. For the first part, the system styrene/acrylonitrile/$ZnCl_2$ was chosen. In the CT theory, acrylonitrile, in contrast to nucleophilic monomers, is a weak electrophilic monomer. Introduction of a Lewis acid increases its acceptor character. An expression of the greater acceptor strength is increased reactivity toward the nucleophilic styrene (St), which shows up in copolymerization as an increase of the overall polymerization rate by increasing the cross-propagation rates.

Furthermore, for the monomer pairs St/maleic anhydride (MAn) and isobutyl vinyl ether/MAn, most of the MAn was bound as a complex when the concentration of the nucleophilic monomer was increased, while the concentration of free MAn was reduced. Under these conditions the addition products of the initiating radical with the monomer complex should be found in the gas chromatogram.

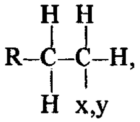
EXPERIMENTAL

Styrene, vinyl isobutyl ether, and acrylonitrile were purified and dried by the usual procedures.

The synthesis of the acrylonitrile/$ZnCl_2$ complex was performed in the following manner: A given amount of $ZnCl_2$ was freed of water during 8 h at 320°C *in vacuo.* Subsequently, an excess of acrylonitrile was condensed into an evacuated ampule containing dried $ZnCl_2$, under its own vapor pressure. After warming up to ambient temperature, argon was blown through the ampule, and the temperature raised to 40-50°C. The zinc chloride dissolved, and a solution of the acrylonitrile/zinc chloride complex was formed in an excess of acrylonitrile. On cooling to ambient temperature, long, colorless, needle-shaped crystals precipitated [10]. The reactivity was determined by the method of Giese [7, 8], which is based on the addition of alkyl radicals, formed by the reaction of alkylmercuric salts with sodium borohydride, to competing alkenes present in the ampule in a fixed ratio. The ratio of the products formed during the addition reaction is determined by gas chromatography. The reactions shown in Scheme 1 take place.

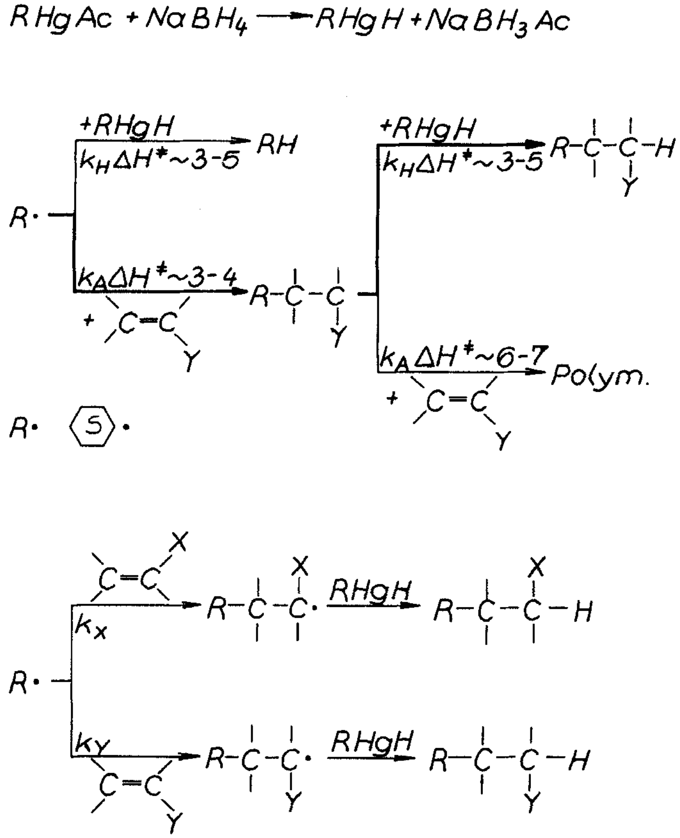
The reaction can be controlled to prevent the propagation reaction of the polymer chain. The initiating species are identified by gas chromatography after hydrogenation.

The experimental procedure to identify the hydrogenated initiating species,



$$R-\overset{H}{\underset{H}{C}}-\overset{H}{\underset{x,y}{C}}-H,$$

which has been slightly modified by us [9], is as follows. Cyclohexylmercuric acetate (CHMA) was added at first to the pure alkenes dissolved in an excess of chloroform at 293 K in the presence of sodium borohydride



SCHEME 1.

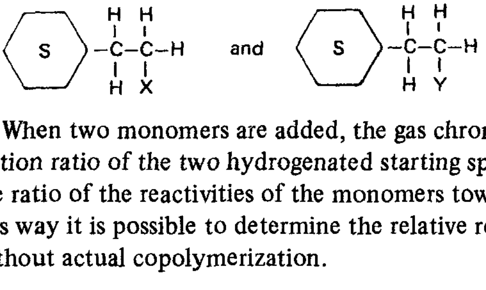
($NaBH_4$). For instance: 3 mmol (1.03 g) of CHMA were reacted under argon with 150 mmol of the corresponding alkene in 15 mL chloroform. To convert MAn, we dissolved 30 mmol (2.94 g). After dissolving the monomer, 3 mmol (0.114 g) $NaBH_4$, dissolved in 5 mL ethanol, was added within a short time. After filtration of the separated mercury, the reaction was analyzed by gas chromatography either directly or after dissolution in chloroform and separation of the boric acid derivatives by the addition of aqueous sodium hydroxide.

The addition products of the cyclohexyl radical to the alkenes were characterized by gas chromatography. The gas chromatograph was a Chromatron, GDR, Type G-CHF 18,3, used under the following conditions:

Column	4 m, 10% SE 52 (a silicon rubber) on Porolite
Detector	FID
Temperature program	60 to 280°C at 12°C/min followed by a 20-min isothermal postperiod
Carrier gas	Ar, 0.75 kg/cm^2
Combustion gas	H_2, 0.15 kg/cm^2
Evaporation temperature	340°C
Temperature at end of column	330°C

The experimental conditions of Giese [7] were modified in that $NaBH_4$ was dissolved in ethanol because chloroform is a poor solvent for $NaBH_4$.

To determine the relative reactivities, we added two alkenes to the reaction mixture in a concentration ratio to give high enough concentrations of the two addition products for chromatographic demonstration.



When two monomers are added, the gas chromatogram shows the concentration ratio of the two hydrogenated starting species, which corresponds to the ratio of the reactivities of the monomers toward the primary radical. In this way it is possible to determine the relative reactivity of monomer pairs without actual copolymerization.

RESULTS AND DISCUSSION

In accord with the investigations of Giese and Meixner [8], the reactivities k of some monomers were first determined relative to St with $k_{\mathrm{rel}} = 1$.

The competitive constants of the radical addition to the alkenes were calculated by

$$\frac{k_1}{k_2} = \frac{[\text{Alkene 2}] \cdot [\text{Adduct 1}]}{[\text{Alkene 1}] \cdot [\text{Adduct 2}]} \tag{1}$$

from the concentration ratios of the corresponding alkenes and the resulting adducts. The relative rate constants were determined for each alkene pair at a number of different initial molar ratios. The initial concentrations of the alkenes were chosen according to the expected reactivities. Cyclohexyl and butyl radicals were used; their preparation was analogous to that of the cyclohexyl radical. MAn is an exception. Because of the high reactivity to be expected, a direct precise measurement with St as reference monomer was not possible. Hence, the reactivity of each monomer was determined with methyl methacrylate (MMA). The reactivity of MMA lies between St and MAn, so that the relative rate constant of St with MAn can be obtained by adding the relative rate constant for St with MMA to that for MAn with MMA. This method seems to have considerable potential, since very reproducible results were obtained by use of acrylonitrile as a further intermediate reference monomer for the reactivity of MAn. The measured values are listed in Tables 1 and 2.

The relative reactivities obtained are in good accordance with expectations, both with regard to order and magnitude. Data from Giese and Meixner [13] show comparable values. An exception is vinyl acetate, with an addition rate that is not of the expected magnitude.

To correlate the measured relative rate constants with the Q and e values of Alfrey and Price,

$$k_{ij} = P_i Q_j \exp(-e_i e_j), \tag{2}$$

from data of the copolymerization of these monomers, we have inserted the relative reactivities k_{rel} as k_{ij} into the equation, and kept P_i constant:

$$\log k_{\mathrm{rel}} - \log Q_j = \mathrm{const} - \frac{e_i}{2.303} e_j. \tag{3}$$

The graphs of $\log k_{\mathrm{rel}} - \log Q_j$ versus e_i in Figs. 1 and 2 show a good linear relation between the radical reactivities and the Q-e values. An e_i of -2.7 for the cyclohexyl and of -2.2 for the butyl radical were obtained from the slopes. Since, by definition, e values indicate something about the influence of polar effects, these values are consistent with the expected nucleophilic character of alkyl radicals. That these radicals react more easily with electrophilic than with nucleophilic alkenes, notwithstanding the higher resonance stabilizaton of the alkyl or benzyl radicals, can be attributed to their nucleophilicity.

In order to see whether the method of Giese [9] is suitable to detect differences in reactivity due to changes of the molecule, measurements of uncom-

TABLE 1. Relative Reactivities of Alkenes in the Reaction with the Cyclohexyl Radical (related to styrene, k = 1)

Monomer	Reference monomer	e^a	k_{rel}
Isobutyl vinyl ether	Styrene	-1.59	0.002
α-Methylstyrene	Methyl methacrylate	-1.27	0.45
Vinyl acetate	Styrene	-0.22	0.047
Styrene		-0.8	1.000
Methyl methacrylate	Styrene	0.4	8.3
Acrylonitrile	Styrene	1.2	120
Maleic anhydride	Methyl methacrylate	2.25	820
Maleic anhydride	Acrylonitrile	2.25	860

[a] Alfrey-Price *Q-e* scheme.

plexed and of $ZnCl_2$-complexed acrylonitrile with the cyclohexyl radical were performed with St as reference monomer. The following results were obtained.

The relative rate constant for the addition of the cyclohexyl radical to acrylonitrile complexed with zinc chloride was 2.25 times higher than with uncomplexed acrylonitrile. It should be noted that only about 25% of the acrylo-

TABLE 2. Relative Reactivities of Alkenes in the Reaction with the *n*-Butyl Radical (related to styrene, k = 1)

Monomer	Reference monomer	e^a	k_{rel}
Styrene		-0.8	1.000
Methyl methacrylate	Styrene	0.4	4.8
Acrylonitrile	Styrene	1.2	75
Maleic anhydride	Methyl methacrylate	2.25	180
Maleic anhydride	Acrylonitrile	2.25	160

[a] Alfrey-Price *Q-e* scheme.

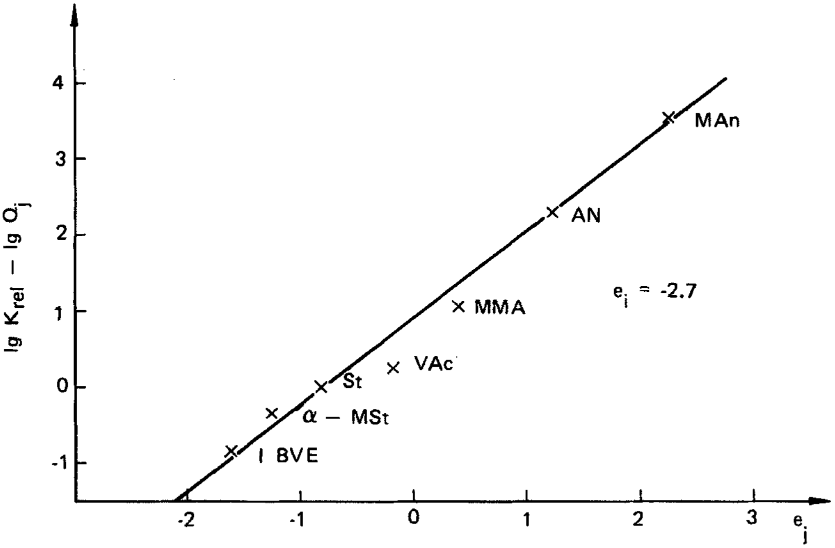


FIG. 1. Correlation between Q and e values of the alkenes and their relative reactivity versus the cyclohexyl radical. IBVE: Isobutyl vinyl ether, α-MSt: α-methylstyrene, St: styrene, VAc: vinyl acetate, MMA: methyl methacrylate, AN: acrylonitrile, MAn: maleic anhydride.

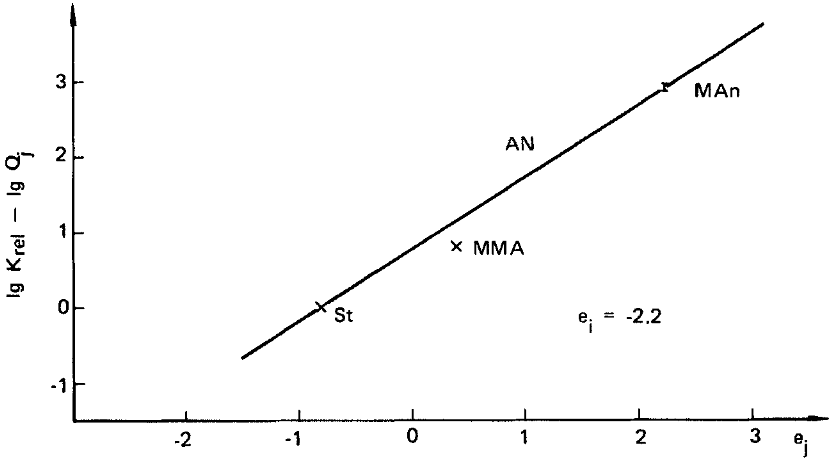


FIG. 2. Correlation between Q and e values of the alkenes and their relative reactivity versus the n-butyl radical. Abbreviations as in Fig. 1.

nitrile is present as complex. Taking into account the fraction of the complex resulted in a reactivity of the acrylonitrile/$ZnCl_2$ system of 2160 (rate constant for the addition of the cyclohexyl radical to St, $k = 1$). This would correspond to an 18-fold increase of reactivity compared to free acrylonitrile and to a threefold reactivity increase for MAn, which is well known to be very reactive toward a donor radical.

No additional peaks that might reflect complex addition of a styrene/acrylonitrile charge-transfer complex were found in the gas chromatogram.

These findings demonstrate that the Giese method is suitable for evaluating changes of monomer reactivities toward donor radicals.

The nucleophilic character of the cyclohexyl radical requires preferred addition to the electrophilic monomer if two monomers of different donor power are used. This leads to hindrance of the addition of the CT complex compared to the uncomplexed electrophilic monomer, and even more strongly to that of the nucleophilic monomer.

Because of the observed high rates and the low complex concentrations (compared to the addition of the uncomplexed monomers), the assumption of the participation of the monomer complex in the copolymerization supposes increased reactivity of the monomer complexes. Thus addition products of the CT complex at the cyclohexyl radical have to be found in every case, while the addition of the nucleophilic monomer should be less probable. Nevertheless, no addition of the cyclohexyl radical to the monomer complex was found by us in the case of the St/MAn monomer pair [9]. Besides a larger excess of cyclohexyl/MAn adducts, cyclohexyl/St adducts were also obtained. The ratio of both adduct concentrations corresponded approximately to the expected reactivity ratio of the monomers toward the nucleophilic cyclohexyl radical [9].

In the present work the concentration of uncomplexed MAn was decreased in favor of the complexed monomer by increasing the styrene concentration relative to MAn. Furthermore, the isobutyl vinyl ether-MAn monomer pair was found to have a manyfold higher complexing constant. Accordingly, the free MAn concentration decreased even more, and the CT-complex concentration in the reaction mixture increased.

Reactions of St/MAn systems were performed at different compositions. The CT complex which is generated from both monomers can be characterized with regard to the strength of the CT interaction by determination of the complex formation constant. For this system a value of $k = 0.32$ L/mol was reported by several authors [11, 12]. For the concentration ratios in question, the MAn equilibrium concentrations are as shown in Table 3 (see also Eq. 4). The reactions of such mixtures with cyclohexyl radicals suggest that reactions of the CT complex with the radical is possible.

TABLE 3. Complex and MAn Equilibrium Concentrations in the System MAn/Styrene at Different Mole Ratios (calculated by Eq. 4)

		[MAn]		
[MAn] : [St]	[C], mol/L	Total, mol/L	Free, mol/L	Free, %
1:10	0.276	0.48	0.204	42.5
1:20	0.27	0.39	0.12	31
1:30	0.2	0.28	0.08	28.6
1:40	0.145	0.205	0.06	29

$$[C] = \frac{[D_0] + [A_0] + 1/k}{2} - \left(\frac{[D_0] + [A_0] + 1/k}{2}\right)^2 - [D_0]\,[A_0] \qquad (4)$$

The MAn equilibrium concentration calculated with the help of Eq. (4) [14] is, for example, 0.06 mol/L at a ratio of 1:40.

Accordingly, 71% of MAn is present as a CT complex with St. Assuming that this complex adds to the cyclohexyl radical, an adduct compound ought to be generated with a gas chromatography retention time different from those of products derived from the individual monomers. Since this was not observed, structures of the adduct radicals of the form C_6H_{11}-MAn-St or C_6H_{11}-St-MAn can be excluded. It follows that the complex cannot be as reactive as others have assumed, or else it would add to the cyclohexyl radical.

The addition of the radical to the complex can, therefore, only occur by decomposition of the complex, and the MAn-adduct radical and St are generated:

$$C_6H_{11}^{\bullet} + (\text{St-MAn}) \longrightarrow C_6H_{11}\text{MAn}^{\bullet} + \text{St}. \qquad (5)$$

A value of 1.29 L/mol is reported as the CT-complex formation constant for the isobutyl vinyl ether/MAn monomer pair [4], which is also confirmed by other authors. In line with the large difference between the *e* values of these monomers, it can be seen that this is a system with the highest known CT interaction of two alkenes. Also, in this case the donor was used in excess to maximize the CT-complex fraction of MAn (Table 4).

TABLE 4. Dependence of the Fraction of Uncomplexed MAn on the Mole Ratio of the Monomers MAn and Isobutyl Vinyl Ether (IBVE)

		[MAn]		
[MAn] : [IBVE]	[C], mol/L	Total, mol/L	Uncomplexed, mol/L	Uncomplexed, %
1:11.7	0.34	0.4	0.06	15
1:100	0.059	0.066	0.007	11

For the reaction of this system with the cyclohexyl radical, in which addition of the complex should be easier, the adduct GC peak of MAn was observed only at a low donor:acceptor ratio and both adduct peaks at a higher ratio (1:100).

Again, this complex does not add to the cyclohexyl radical. Because of the large reactivity differences between the two monomers, no direct quantitative conclusions were possible since larger differences in the *e* values of the monomers must lead to considerable reactivity differences relative to the nucleophilic cyclohexyl radical, according to the mechanism discussed by Giese and Meister [7].

Because the radicals used are strong donors, one might assume that the addition of the complex to the radicals does not occur. However, since the GC peaks of the adducts of the donor monomers St and isobutyl vinyl ether were observed and those of the CT complexes were not, this assumption cannot be valid. Although the method used by us offers the possibility of confirming the change of reactivity of the CT-monomer systems caused by complexation, it was not possible to do so.

REFERENCES

[1] N. G. Gaylord, *J. Polym. Sci., D4,* 209 (1970).
[2] D. Fles, *Polym. Bull. (Berlin), 2,* 527 (1980).
[3] Z. M. Rzaev, I. P. Zeinalov, L. V. Medjakova, A. J. Babaev, and M. M. Agaev, *Vysokomol. Soedin., Ser. A, 23,* 614 (1981).
[4] M. Hallensleben, *Makromol. Chem., 144,* 267 (1971).
[5] K. Dodgson and J. R. Ebdon, *Eur. Polym. J., 13,* 791 (1977).

[6] C. H. Bamford, *Plaste Kautsch.*, *29*, 137 (1982).
[7] B. Giese and J. Meister, *Chem. Ber.*, *110*, 2588 (1977).
[8] B. Giese and J. Meixner, *Angew. Chem.*, *92*, 215 (1980).
[9] M. Raetzsch and V. Steinert, *Makromol. Chem.*, *185*, 2411 (1984).
[10] M. Imoto, T. Otsu, and M. Nakabayashi, *Ibid.*, *65*, 144 (1963).
[11] E. Tsuchida, T. Tomono, and H. Sano, *Ibid.*, *151*, 2445 (1972).
[12] M. Raetzsch and G. Schicht, *Acta Polym.*, *32*, 300 (1981).
[13] B. Giese and J. Meixner, *Angew. Chem.*, *91*, 167 (1979).
[14] M. Arnold, DSc Thesis, Technical University Leuna-Merseburg, October 8, 1980, p. 34.

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