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**Citation for published version (APA):**

Meer, van der, R., Aarts, M. W. A. M., & German, A. L. (1980). Effect of solvent on the copolymerization of ethylene and vinyl acetate. *Journal of Polymer Science, Polymer Chemistry Edition*, 18(4), 1347-1357. <https://doi.org/10.1002/pol.1980.170180418>

**DOI:**

[10.1002/pol.1980.170180418](https://doi.org/10.1002/pol.1980.170180418)

**Document status and date:**

Published: 01/01/1980

**Document Version:**

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

**Please check the document version of this publication:**

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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# Effect of Solvent on the Copolymerization of Ethylene and Vinyl Acetate

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## Synopsis

The ethylene ( $M_1$ )-vinyl acetate ( $M_2$ ) copolymerization at 62°C and 35 kg/cm<sup>2</sup> with  $\alpha,\alpha'$ -azobisisobutyronitrile as initiator has been studied in four different solvents, viz., *tert*-butyl alcohol, isopropyl alcohol, benzene, and *N,N*-dimethylformamide. The experimental method used was based on frequent measurement of the composition of the reaction mixture throughout the copolymerization reaction by means of quantitative gas chromatographic analysis. Highly accurate monomer reactivity ratios have been calculated by means of the curve-fitting *I* procedure. The observed dependence of the *r* values on the nature of the solvent is surprisingly large and can be correlated with the volume changes (= excess volumes) observed on mixing vinyl acetate (VAc) with the relevant solvent. An increased hydrogen bonding or dipole-dipole interaction through the carbonyl moiety of the acetate side group of VAc, induces a decreased electron density on the vinyl group of VAc, which in turn leads to a decreased VAc reactivity. The differences among the overall rates of copolymerization in the various solvents can be interpreted in terms of a variable chain transfer to solvent and the rate of the subsequent reinitiation by the solvent radical. In the case of benzene, complex formation is believed to play an important part.

## INTRODUCTION

During a long period it has been assumed that in free radical polymerization reactions the nature of the solvent would not affect<sup>1-3</sup> the chain propagation constant  $k_p$ . Also in copolymerization the effect of solvent on the monomer reactivity ratios (*r* values) was believed to be negligible. During the last decade, however, many published data<sup>4-14</sup> on solvent-dependent polymerization as well as copolymerization provided evidence to the contrary. In order to investigate the effect of solvent on  $k_p$ , two basically different methods are available: (1) measuring the separate contributions of  $k_p$  and  $k_t$  (= termination rate constant) to the change of the overall rate of homopolymerization by means of the rotating sector technique<sup>15</sup>; (2) measuring the change of the monomer reactivity ratios by copolymerizing a binary combination. Unfortunately, either method has its characteristic drawbacks. In the first method it is always implicitly assumed that the overall rate of polymerization remains unaffected by chain transfer to solvent, and a possibly slow subsequent reinitiation by the solvent radical. In the second method only an effect on ratios of chain propagation rate constants can be measured. This requires the choice of a comonomer, the reactivity of which is not affected by the nature of the solvent. For this purpose, styrene has often been chosen as "reference" monomer,<sup>5-7,11,12,14</sup> as for instance in case of the intensively investigated copolymerization with methyl methacrylate,<sup>6,14</sup>

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where the effect of solvent on the measured  $r$  values invariably has been ascribed to a varying influence of different solvents on the methyl methacrylate reactivity. However, according to Burnett et al.<sup>8</sup> the chain propagation rate constant of the styrene homopolymerization is also affected by the nature of the reaction medium. In those cases, where styrene was not chosen as "reference" monomer,<sup>9,10,13</sup> the variation of the  $r$  values was mostly interpreted in terms of an influence of solvent on the more polar monomer only. Most physical interpretations are based on hydrogen-bonding abilities, polarization, dipole-dipole interactions, microphase separation of the copolymer, complex formation, and stabilization of the growing chains. Satisfactory quantitative correlations with one of these physical quantities have never been given up to now, possibly since the most obvious reference monomer, i.e., ethylene, was never used because of practical difficulties. The previously reported<sup>16</sup> method of "sequential sampling," based on quantitative gas-liquid chromatography (GLC), is very suitable for the study of gaseous monomers, as, for example, ethylene.

In the present investigation ethylene has been chosen as reference monomer in the copolymerization with vinyl acetate in four different solvents, i.e., *tert*-butyl alcohol, isopropyl alcohol, benzene, and *N,N*-dimethylformamide. Highly accurate monomer reactivity ratios have been obtained by means of the recently described curve-fitting  $I$  procedure,<sup>17</sup> which is based on the integrated copolymer equation and considers experimental errors in both measured variables. The large effect of solvent on both  $r$  values is correlated successfully with the measured volume changes (excess volumes) observed on mixing the monomer vinyl acetate with the various solvents. Furthermore, a semiquantitative comparison of the differences among the overall rates of copolymerization in the various solvents will be given.

## EXPERIMENTAL

### Materials

The specifications of the monomers ethylene (Eth) and vinyl acetate (VAc) and the radical initiator  $\alpha,\alpha'$ -azobisisobutyronitrile (AIBN) have been reported elsewhere.<sup>16,18</sup>

**Solvents:** Chemically pure isopropyl alcohol (IPA) (Shell), containing <0.5% impurities, benzene (Bz) pro analysis (Merck), containing <0.03% water and <0.0005% thiophene, and *N,N*-dimethylformamide (DMF) pro analysis (Fluka), being at least 99.5% pure, were used without further purification, except for the degassing just before use. Specifications of *tert*-butyl alcohol (TBA) have been reported elsewhere.<sup>18</sup>

### Copolymerization

All Eth ( $M_1$ )-VAc ( $M_2$ ) free radical copolymerizations were carried out at  $62 \pm 0.1^\circ\text{C}$  and  $35 \text{ kg/cm}^2$  with AIBN as initiator. The experimental conditions are summarized in Table I. Phase separation was not observed during any of these copolymerizations.

During the entire course of a copolymerization reaction the monomer feed composition was determined by means of quantitative GLC.<sup>16</sup> The relevant

TABLE I  
Experimental Conditions of the Copolymerization of Ethylene ( $M_1$ ) with Vinyl Acetate ( $M_2$ ) in Various Solvents<sup>a</sup>

Solvent	Initial monomer feed ratio, $q_0$	Final monomer feed ratio	Conversion based on $M_2$ (%)	Number of observations	Initiator concentration (mmole/dm <sup>3</sup> )	Total initial monomer concentration (mole/dm <sup>3</sup> )
IPA	3.0722	3.2040	13.92	23	Varying from 1.5 to 4.0	Varying from 1.2 to 2.5
	2.0760	2.1875	16.54	19		
	1.5142	1.6326	25.08	20		
	1.1237	1.2163	24.89	23		
	0.9012	0.9770	25.10	22		
	0.4467	0.5192	37.15	21		
	0.2944	0.3342	34.18	20		
	0.1809	0.2199	45.92	21		
	0.1058	0.1322	50.61	23		
Bz	3.8329	3.8946	6.20	36	12.5	1.23
	3.4519	3.5080	7.69	67		1.41
	2.2411	2.2959	9.36	61		1.24
	1.0583	1.0952	12.34	75		1.31
	0.7251	0.7459	10.87	55		1.32
	0.4515	0.4692	14.42	65		1.29
	0.2300	0.2457	21.45	62		1.25
DMF	4.0343	4.1402	25.72	36	3.6	1.28
	2.1319	2.1753	19.07	33		1.19
	1.3966	1.4311	23.52	29		1.22
	0.9594	0.9931	30.43	33		1.25
	0.7274	0.7625	37.84	32		1.32
	0.3951	0.4146	36.63	36		1.24

<sup>a</sup> Experimental conditions of the nine kinetic experiments in TBA (221 observations) have been given elsewhere.<sup>16</sup>

GLC conditions for the systems investigated were for Eth-VAc in TBA and IPA, identical and reported elsewhere<sup>16</sup>; for Eth-VAc-Bz, column temperature,  $80 \pm 0.1^\circ\text{C}$ ; detector temperature,  $110^\circ\text{C}$ ; stationary phase, 10% by wt squalane on Chromosorb W, mesh 100-120 (Johns Manville); and for Eth-VAc-DMF, column temperature,  $80 \pm 0.1^\circ\text{C}$ ; detector temperature,  $160^\circ\text{C}$ ; stationary phase, 15% by wt Carbowax 6000 on Chromosorb P, mesh 80-100 (Johns Manville).

The isolation and purification of the copolymers proceeded analogously to the method reported earlier,<sup>16</sup> except for the copolymers obtained in Bz, which were isolated by precipitation in *n*-hexane.

### Estimation of Monomer Reactivity Ratios

The  $r$  values have been evaluated by means of the recently described curve-fitting  $I$  procedure,<sup>17</sup> assuming that the relative measurement errors in the GLC peak areas of Eth, VAc, and the relevant solvent are 1.0, 1.0, and 1.5%, successively. In this method, besides very accurate  $r$  values, the relevant standard deviations are also calculated.<sup>17</sup>

### Density Measurements

Density measurements have been carried out by means of a vibrating-tube densimeter, i.e., a Paar Precision Density Meter, model DMA 10. The principle of this instrument is based on the measurement of the natural frequency of a hollow oscillator—a U-shaped tube—when filled with different liquids.<sup>19</sup> The oscillator is water jacketed and thermostated by circulating water from a constant-temperature bath. In this way temperature fluctuations are minimized to  $<0.005^{\circ}\text{C}$ . Under these conditions an accuracy of the measured density of  $<2.5 \times 10^{-4} \text{ g/cm}^3$  may be obtained. The densimeter was calibrated with the aid of pure water<sup>20</sup> and air.<sup>20</sup>

Excess volumes are derived from the densities of the binary mixtures by means of the following expression:

$$V^E = [(1 - x_2)M_1 + x_2M_2]/d_m - [(1 - x_2)M_1/d_1 + x_2M_2/d_2]$$

where  $M_1$  and  $M_2$  are the molecular weights of the pure liquids,  $d_1$  and  $d_2$  are the respective densities,  $x_2$  is the mole fraction of component 2, and the subscript  $m$  denotes mixture.

## RESULTS AND DISCUSSION

### Overall Rate of Copolymerization

The great number of reaction rate constants to be considered for the description of the overall rate of reaction in copolymerization makes a detailed quantitative consideration a complicated matter. Therefore, in this article a semiquantitative comparison of the overall rates of copolymerization,  $R_p$ , of the Eth-VAc copolymerizations in the various solvents will be given. The decomposition rate of AIBN is generally supposed to be unaffected by a change of solvent. But in literature also contradictory findings were reported.<sup>21,22</sup>

Estimates of  $R_p$  for each separate kinetic experiment are calculated by dividing the total molar conversion of Eth and VAc by the reaction time elapsed from the actual start of the copolymerization reaction (i.e., after the induction period) until the moment the kinetic experiment was stopped. For the purpose of comparison it is preferable to consider  $R_p/\sqrt{I_0}$ , in which  $I_0$  is the initial initiator concentration, as—under certain conditions—in homopolymerization, as well as in copolymerization:  $R_p \sim \sqrt{I}$ . In Figure 1,  $R_p/\sqrt{I_0}$  has been plotted versus the mole fraction Eth in the monomer feed, for all solvents presently involved, except IPA. During experiments using the latter solvent, only qualitative information was recorded. Figure 1 reveals that  $R_p/\sqrt{I_0}$  decreases in these solvents as the Eth content in the monomer feed increases, while previous studies<sup>16,18</sup> have shown that the number-average degree of polymerization,  $\bar{P}_n$ , also decreases with increasing Eth content in the copolymer being formed. These phenomena can be explained in terms of an increased propensity for chain transfer to monomer, polymer, or solvent as the Eth content in the feed increases. The reactive Eth macroradical more easily abstracts a hydrogen atom from any chain transfer agent available than does the relatively less reactive VAc macroradical, while the subsequent reinitiation by the transfer radical may be substantially slower than the various propagation rates. Furthermore, an increasingly retarding effect at higher Eth content in the feed also may be ascribed to the well-known

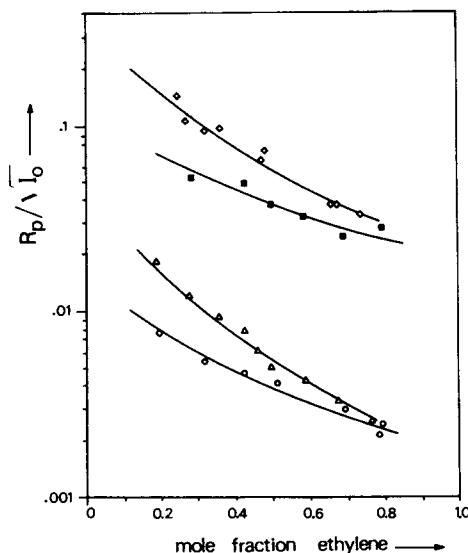


Fig. 1. The "reduced" overall rate of copolymerization,  $R_p/\sqrt{I_0}$ , versus the mole fraction ethylene in the monomer feed for the ethylene-vinyl acetate copolymerization in various solvents: ( $\diamond$ ) *tert*-butyl alcohol, ( $\circ$ ) benzene, ( $\Delta$ ) acetone, and ( $\blacksquare$ ) *N,N*-dimethylformamide.

phenomenon of backbiting, which plays an important part in the Eth homopolymerization.<sup>23</sup>

A comparison of the values of  $R_p/\sqrt{I_0}$  and  $\bar{P}_n\sqrt{I_0}$  (in homopolymerization the kinetic chain length is inversely proportional to  $\sqrt{I}$ ) for the solvents involved, at 80 mole % VAc in the feed, is presented in Table II. A strong decrease of the "reduced"  $\bar{P}_n$  is observed in the order TBA > IPA  $\geq$  DMF, while the "reduced"  $R_p$  is comparatively constant for these three solvents. This can be interpreted in terms of an increased chain transfer to solvent in the order TBA < IPA  $\leq$  DMF while the rate constant of the subsequent reinitiation by the solvent radical is of the same order of the various  $k_p$ 's involved. These findings appear to be in agreement with literature values<sup>24</sup> of the chain transfer constant,  $C_s = k_{tr}/k_p$ , in the VAc homopolymerization, as shown in Table II. For copolymerizations in Ac,  $R_p/\sqrt{I_0}$  is substantially lower than in case of the three preceding solvents, while  $\bar{P}_n\sqrt{I_0}$  as well as  $C_s$  are of the same order of magnitude as for copolymers formed in DMF. Evidently, reinitiation by an Ac radical is considerably slower

TABLE II

"Reduced" Overall Rate of Copolymerization and Number-Average Degree of Polymerization for Copolymers Formed in Various Solvents at 80 mole % Vinyl Acetate in the Feed

Solvent	$R_p/\sqrt{I_0}$ ( $\times 10^{+2}$ ) <sup>a</sup>	$\bar{P}_n$	$\bar{P}_n\sqrt{I_0}$ <sup>a</sup>	$C_s$ ( $\times 10^{+4}$ ) <sup>b</sup>
TBA	110	840	1060	1.3
IPA	ca. 100	130	165	44.6
DMF	70	76	145	50.0
Bz	8	128	455	0.7
Ac	11	67	200	42.0

<sup>a</sup>  $I_0$  in mmole/dm<sup>3</sup>.

<sup>b</sup> Chain transfer constant for vinyl acetate homopolymerization.<sup>24</sup>

than by a DMF radical (retardation in Ac). In Bz,  $R_p/\sqrt{I_0}$  is still lower, while the reduced  $\bar{P}_n$  is higher than for solvents like DMF and Ac.

An explanation in terms of chain transfer is not valid for copolymerizations in Bz, as is indicated by the low  $C_s$  value.<sup>24</sup> In the case of Bz substantial evidence exists for complex formation with radicals, which appears to lead to a decreased radical reactivity.<sup>25</sup> In (co)polymerization this will show up in a decrease of  $k_p$  and as a consequence also a decrease of  $R_p$  and  $\bar{P}_n$  (as compared with other low-transfer solvents like TBA). This interpretation of our findings on the Eth-VAc copolymerization in Bz is supported by the anomalous overall rate of homopolymerization of styrene in Bz, where exceptionally low values of  $R_p$  and  $\bar{P}_n$  also were ascribed to a complex formation between the polystyryl radical and Bz.<sup>8</sup> In addition, the present results on the Eth-VAc copolymerization in Bz are for the greater part analogous to the findings of Wisotksy and Kober,<sup>26</sup> who carried out a comparative study on this binary copolymerization in some aliphatic and aromatic solvents, with regard to copolymer yield and number-average molecular weight.

Finally, to summarize it can be stated that the differences among the overall rates of copolymerization as well as among the number-average molecular weights of the copolymers formed during the Eth-VAc copolymerization in various solvents are mainly governed by chain transfer to solvent and the subsequent reinitiation, except for Bz, where the decreased overall rate of copolymerization appears to be affected by complex formation of propagating macroradicals with Bz.

### Monomer Reactivity Ratios

The Eth ( $M_1$ )-VAc ( $M_2$ ) copolymerization has been carried out in four different solvents: TBA, IPA, Bz, and DMF. The calculated  $r$  values of the various systems, summarized in Table III, reveal an unexpectedly strong effect of the nature of the solvent. The calculated standard deviations, as shown by Table III, and the plotted confidence regions of the  $r$  values, as shown in Figure 2, do not overlap, from which it may be concluded that the observed differences among the  $r$  values pertaining to the various systems are significant. One of the most striking facts is the simultaneous increase of  $r_1$  with the decrease of  $r_2$ , which also appears from the practical constancy of the product of the  $r$  values,  $\pi$  (see Table III).

An explanation of these results has been developed along the following lines. Primarily, it seems logical to focus on finding correlations between the variation of the  $r$  values and physical quantities of the solvent. The  $1/r_1$  and  $r_2$  values

TABLE III  
Calculated Monomer Reactivity Ratios for the Ethylene ( $M_1$ )-Vinyl Acetate ( $M_2$ )  
Copolymerization in Various Solvents

Solvent	$r_1$	$r_2$	$\pi = r_1 r_2$
TBA	$0.74 \pm 0.01^a$	$1.50 \pm 0.01^a$	$1.11 \pm 0.02$
IPA	$0.77 \pm 0.01$	$1.485 \pm 0.006$	$1.14 \pm 0.02$
Bz	$0.80 \pm 0.02$	$1.39 \pm 0.02$	$1.11 \pm 0.04$
DMF	$0.92 \pm 0.01$	$1.13 \pm 0.01$	$1.04 \pm 0.02$

<sup>a</sup> Estimated standard deviations.

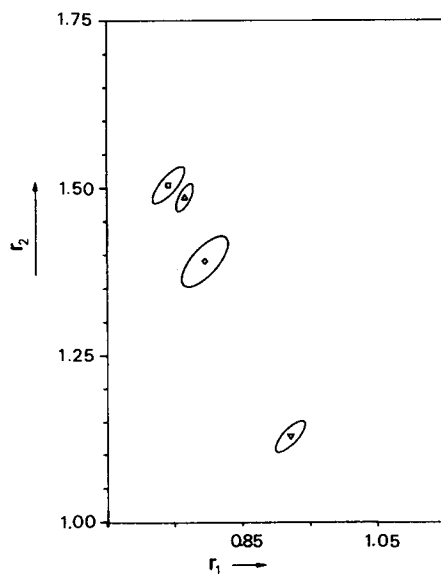


Fig. 2. Confidence regions for  $\alpha = 95\%$  for the  $r$  values pertaining to the ethylene ( $M_1$ )-vinyl acetate ( $M_2$ ) copolymerization in four different solvents: ( $\square$ ) *tert*-butyl alcohol, ( $\Delta$ ) isopropyl alcohol, ( $\diamond$ ) benzene, and ( $\nabla$ ) *N,N*-dimethylformamide.

appear to lack any correlation with  $E_T$  values,<sup>27</sup> expressing the ability of a solvent molecule to donate a hydrogen atom, or with the solubility parameter<sup>28</sup>  $\delta$ , or with the separate contributions to  $\delta$ , i.e., the solubility parameter due to dispersion forces,<sup>29,30</sup>  $\delta_d$ , the solubility parameter due to dipole forces,<sup>29,30</sup>  $\delta_p$ , and the solubility parameter due to hydrogen bonding,<sup>29,30</sup>  $\delta_h$ , as shown in Table IV. Although the dielectric constants<sup>31</sup> of the solvents,  $\epsilon$ , yield a satisfactory correlation with  $1/r_1$  for the more polar solvents like TBA, IPA, and DMF, it does not for Bz, as shown by Figure 3.

Therefore, it would appear to be more meaningful to search for physical quantities expressing those combined interactions between solvents and monomers which may be expected to be responsible for major effects on monomer

TABLE IV  
Vinyl Acetate Reactivity ( $1/r_1$  and  $r_2$ ) in Ethylene ( $M_1$ )-Vinyl Acetate ( $M_2$ ) Copolymerization Compared with Some Selected Physical Properties of the Solvents Used

Solvent	$1/r_1$	$r_2$	$E_T^a$	Dielectric constant $\epsilon$ (at 25°C) <sup>b</sup>	Solubility parameters			
					$\delta^c$	$\delta_d^d$	$\delta_p^d$	$\delta_h^d$
TBA	1.35	1.50	43.9	10.9	10.7	7.81 <sup>e</sup>	2.8 <sup>e</sup>	7.7 <sup>e</sup>
IPA	1.30	1.49	48.6	20.1	11.9 <sup>f</sup>	7.75 <sup>f</sup>	3.3 <sup>f</sup>	8.5 <sup>f</sup>
Bz	1.25	1.39	34.5	2.3	9.2	8.95	0.5	1.0
DMF	1.08	1.13	43.8	34.8	11.1	8.52	6.7	5.5

<sup>a</sup> Reichardt et al.<sup>27</sup>

<sup>b</sup> Values derived from literature.<sup>31</sup>

<sup>c</sup> Reference 28.

<sup>d</sup> Values given by Hansen and Skaarup.<sup>29,30</sup>

<sup>e</sup> Values for 1-butyl alcohol.

<sup>f</sup> Values for 1-propyl alcohol.



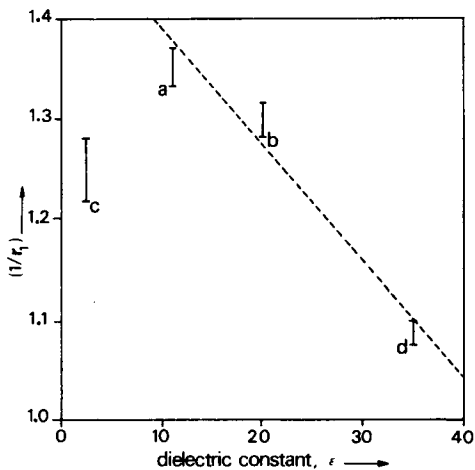


Fig. 3.  $1/r_1$  versus the dielectric constant  $\epsilon$  of the various solvents: (a) *tert*-butyl alcohol, (b) isopropyl alcohol, (c) benzene, and (d) *N,N*-dimethylformamide.

reactivity. In this context it seems to be worthwhile to point out that a possible Eth-solvent interaction will be negligible as compared with the VAc-solvent interaction, and as a consequence the effect of solvent on the  $r$  values may, as a first approximation, be fully ascribed to a variation in the reactivity of the VAc monomer. These are sufficient motives to call attention to the volume changes on mixing VAc with the various solvents. The excess volume  $V^E$  appears to be dependent on both the nature of the particular solvent and the composition of the binary mixture with VAc, as shown in Figures 4 and 5. Therefore, in Figure 6,  $1/r_1$  has been plotted versus  $V^E$ , at a mole fraction VAc of 0.1, which corresponds approximately with the average molar concentration of VAc in the reaction mixture. This graph demonstrates a surprisingly good correlation, which indicates that evidently the excess volumes are characteristic of specific interactions closely connected with the cause of the solvent-dependent variations of VAc monomer reactivity.

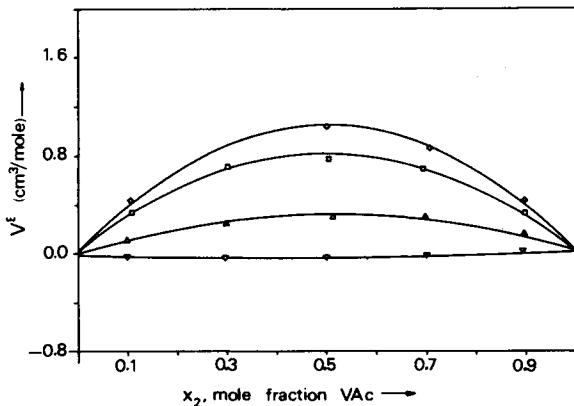


Fig. 4. Excess volumes  $V^E$  versus the mole fraction vinyl acetate ( $x_2$ ) in binary mixtures with various alcohols: ( $\diamond$ ) *tert*-butyl alcohol, ( $\square$ ) isopropyl alcohol, ( $\Delta$ ) ethyl alcohol, and ( $\nabla$ ) methyl alcohol at 62°C.

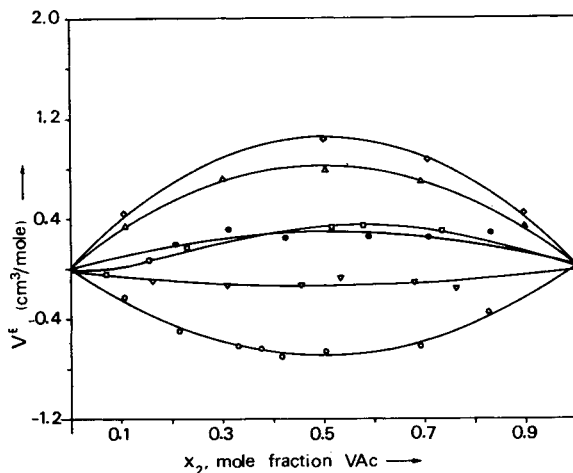


Fig. 5. Excess volumes  $V^E$  versus the mole fraction vinyl acetate ( $x_2$ ) in binary mixtures with various solvents: ( $\diamond$ ) *tert*-butyl alcohol, ( $\Delta$ ) isopropyl alcohol, ( $\bullet$ ) toluene, ( $\square$ ) benzene, ( $\nabla$ ) acetone at 45°C, and ( $\circ$ ) *N,N*-dimethylformamide at 62°C.

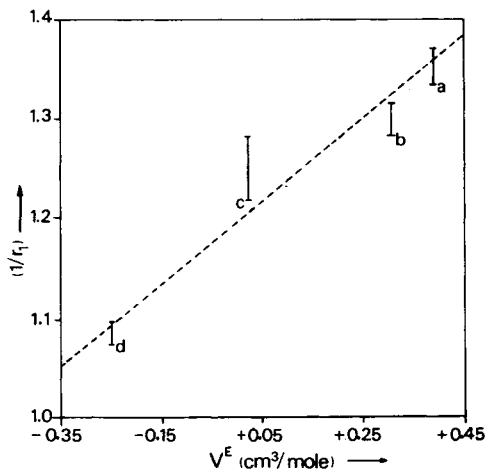
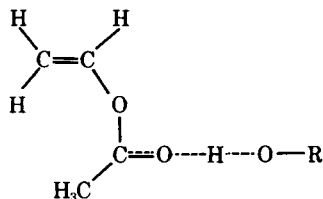


Fig. 6.  $1/r_1$  versus the excess volume  $V^E$  (at mole fraction VAc,  $x_2 = 0.1$ ), for mixtures of vinyl acetate with various solvents: (a) *tert*-butyl alcohol, (b) isopropyl alcohol, (c) benzene, and (d) *N,N*-dimethylformamide.

On mixing VAc with a number of alcohols of increasing acidity, TBA, IPA, ethyl alcohol, and methyl alcohol, decreasing values of  $V^E$  have been observed (cf. Fig. 4), which may be interpreted in terms of an enhanced hydrogen bonding between VAc and alcohol in the order methyl alcohol > ethyl alcohol > IPA > TBA.



Such a hydrogen bonding induces an increased electronegativity on the carbonyl O atom, which in turn enhances the electron-withdrawing character of the entire acetate side group. A decrease in vinyl acetate reactivity due to steric effects cannot be completely excluded. The results of our study of the effect of pressure on Eth-VAc copolymerization in TBA,<sup>32</sup> however, indicate that steric hindrance becomes improbable. If the vinyl acetate addition would be sterically hindered, this reaction would be more strongly accelerated by pressure than the ethylene addition. However, the contrary was found to be true.<sup>32</sup>

In binary mixtures of VAc with various other solvents (see Fig. 5) the observed decrease of  $V^E$ , TBA > Bz > toluene > acetone > DMF, will be caused mainly by an increased dipole-dipole interaction, while in the case of Bz and toluene induced polarization also may lead to interaction(s) through the carbonyl group of VAc. Both types of interaction will enhance the electron-withdrawing character of the acetate side group and lead to a lower electron density on the vinyl group of VAc.

In a study on the reactivity of a homologous series of vinyl esters with Eth<sup>18</sup> and VAc<sup>33</sup> as reference monomers, it has been shown that the vinyl ester monomer reactivity decreases as the electron-withdrawing character of the ester side group increases. These findings fit in exactly with the present results on the solvent-induced shift of the VAc monomer reactivity, as, in both cases, it appears that a decreased electron density on the vinyl group leads to a diminished reactivity of the monomer. According to the terminology employed by Kabanov<sup>34</sup> with regard to chemical activation of monomers, the present findings may be regarded as an intramolecular effect, because the VAc-solvent interaction causes an electron redistribution on the intramolecular bonds of VAc, rather than a (re)orientation of the monomer molecules (intermolecular effect).

## CONCLUSIONS

The present study on the Eth-VAc copolymerization has shown an unexpectedly large effect of the nature of the solvent on both the overall rate of copolymerization and the resulting monomer reactivity ratios.

The differences among the observed overall rates of copolymerization can be interpreted in terms of a solvent-dependent chain transfer in combination with the subsequent reinitiation by the solvent radical being formed. In Bz, however, complex formation between macroradicals and solvent molecules plays a dominant role.

The shift of  $r$  values can be correlated with hydrogen bonding and dipole-dipole interaction between solvent molecules and the more polar comonomer VAc, expressed in terms of excess volumes of binary mixtures of VAc with the respective solvents. An increased interaction between solvent and VAc induces a decreased electron density on the double bond of VAc, which leads to a lower inherent reactivity of VAc.

The observed correlation of  $1/r_1$  with  $V^E$  allows some additional conclusions to be drawn. (1) A concentration-dependent monomer reactivity should be expected. In fact such a phenomenon has already been observed for the VAc-MMA copolymerization in various solvents.<sup>13</sup> (2) Measurement of the intrinsic reactivity of a monomer will be difficult, if not impossible. (3) As monomer-solvent interaction is affected by, e.g., pressure, temperature, and structural

changes within a homologous series of monomers, these variations will inevitably influence the (inherent) monomer reactivity.

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Received September 19, 1978

Accepted July 5, 1979