1128. *Cationic Copolymerisation of 2-Chloroethyl Vinyl Ether with Styrene and with α-Methylstyrene.*

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2-Chloroethyl vinyl ether has been copolymerised with styrene and with α-methylstyrene by means of boron trifluoride complexes and other cationogenic initiators in various solvents. The copolymerisations are found to be non-ideal ($r_1r_2 \neq 1$) and the reactivity ratios differ in the different catalyst–solvent systems. The variations are attributed to the effect of the catalyst counter-anion on the carbonium-ion reactivities. With α-methylstyrene the reactivity ratios show a significant temperature-dependence over the range $-30°$ to 25°, this being believed to be due to appreciable differences in the activation energies of the propagation reactions.

The cationic copolymerisation of 2-chloroethyl vinyl ether (CEVE) with styrene and with α-methylstyrene has been investigated with the initiators and solvents listed in the Table.

EXPERIMENTAL

The monomers were commercial samples (British Drug Houses Ltd.), dried by barium oxide and calcium hydride, purified by two vacuum-distillations, outgassed, and stored in a vacuum-line protected from light. The styrene had b. p. 45°/20 mm., α-methylstyrene b. p. 60°/18 mm., and 2-chloroethyl vinyl ether (CEVE) b. p. 108°/760 mm.; all gave single peaks in a gas–liquid chromatogram.

The fuller's earth was a " natural earth " (Fullers Earth Union 237 D) not activated or dried. Boron fluoride complexes were commercial samples freshly distilled before being made up into stock catalyst solutions.

Solvents were purified by fractional distillation, stored over calcium hydride, and dispensed from the storage vessels through self-filling burettes protected by guard-tubes of silica gel. Catalyst solutions were stored in, and dispensed from, similar protected vessels. The catalyst boron trifluoride–ether complex was insufficiently soluble in ethylene dichloride alone, and was made up in a mixture containing 25% by volume of diethyl ether, resulting in a concentration of 6% by volume of ether in the final reaction mixture.

Reaction procedure was as follows. The desired volumes of monomers (to give a total monomer concentration 2·5M in the reaction mixture) were distilled on the vacuum-line into one arm of a forked reaction vessel of Pyrex glass, each arm consisting of a tube of capacity ~20 ml. Dry air was admitted, and the vessel was detached and stoppered after solvent and catalyst solution had been measured by burette into the other arm. The vessel was then brought to reaction temperature and shaken to mix the reactants. After appropriate reaction times, the polymerisations were stopped by shaking the products with water containing a little potassium hydroxide. Conversions were usually ~20%, but sometimes as high as 40% with copolymers weak in CEVE. The copolymers were isolated by further washing with water, separation from the aqueous phase, and removal of all volatile material at 10^{-4}—10^{-5} mm. This isolation was done quantitatively and the conversion calculated from the yield of copolymer. The copolymer composition was calculated from the chlorine content as determined by Schoninger's semimicro-combustion method.[1]

Copolymer composition curves were determined for 4—8 (usually 6) different initial monomer compositions, and reactivity ratios were calculated from the Mayo–Walling equation.[2] The integrated form of the equation was used for the styrene–CEVE copolymers where the reactivity ratios are so different that the monomer composition changes sharply with conversion. With α-methylstyrene–CEVE copolymers, the differential form of the equation (involving the mean monomer composition) was judged to be adequate, *i.e.*, in these experiments the drift of monomer composition during conversion was small (<7%)—smaller than the drift in other preliminary experiments in which both integral and differential calculations yielded values

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[1] Schoninger, *Microchim. Acta*, 1955, **1**, 123.

[2] Alfrey, Bohrer, and Mark, " Copolymerisation," Interscience Publ., Inc., New York, 1952.

closer than the experimental error. The r-values given in the Table are weighted means calculated by Joshi and Kapur's method.[3] The errors listed give the range of values which includes 60—70% of the intersections on Mayo–Lewis plots.

RESULTS

No rates of copolymerisation were measured. Catalyst concentrations differed in different systems, being chosen to give 20—30% conversion in convenient times. These times varied from 180 min. with the boron trifluoride–ether complex in ether–ethylene dichloride to 1 min. with this complex in nitrobenzene.

Molecular weights were not determined. The intrinsic viscosities (in benzene at 25°) lay in the range 0·035—0·6 dl./g. If the relationship found by Eley *et al.*[4] for homopoly-CEVE is valid for the copolymers, this range indicates molecular weights of 800—15,000.

Copolymers containing $<\sim 40\%$ of CEVE were white, brittle solids. Those richer in CEVE were sticky gums or very viscous oils. The latter decomposed slowly, becoming yellow-brown (noticeable after ~1 week) and eventually black. Hydrogen chloride was released in this decomposition, but unless pumped off remained trapped in the sticky polymer; *e.g.*, homopoly-CEVE had the theoretical chlorine content (33·3%) even when considerably discoloured. Samples were analysed within four days of isolation and gave results reproducible to $\pm 1\%$ of the chlorine content when $\mathrm{Cl} \gtrsim 30\%$ and $\pm 2\%$ when $\mathrm{Cl} \gtrsim 15\%$.

In the Table, the reactivity ratios r_1 and r_2 are defined by

$$\left.\begin{array}{l} \sim\!\sim m_1^+ + M_1 \xrightarrow{k_{11}} \sim\!\sim m_1m_1^+ \\ \sim\!\sim m_1^+ + M_2 \xrightarrow{k_{12}} \sim\!\sim m_1m_2^+ \end{array}\right\} k_{11}/k_{12} = r_1;$$

$$\left.\begin{array}{l} \sim\!\sim m_2^+ + M_2 \xrightarrow{k_{22}} \sim\!\sim m_2m_2^+ \\ \sim\!\sim m_2^+ + M_1 \xrightarrow{k_{21}} \sim\!\sim m_2m_1^+ \end{array}\right\} k_{22}/k_{21} = r_2.$$

TABLE.

Reactivity ratios in cationic copolymerisation of 2-chloroethyl vinyl ether (CEVE) with styrene and with α-methylstyrene. Total monomer concentration = 2·5M.

Temp.	Catalyst	Solvent	r_1	r_2	r_1r_2
		CEVE (1) *and styrene* (2)			
−30°	Fullers earth	$(CH_2Cl)_2$	8·0 ± 1·0	0·06 ± 0·02	0·48 ± 0·22
,,	BF_3–Et_2O	94% $(CH_2Cl)_2$ 6% Et_2O	16·0 ± 1·5	0·04 ± 0·01	0·64 ± 0·22
,,	BF_3–2AcOH	$(CH_2Cl)_2$	30·5 ± 8·0	0·12 ± 0·05	3·66 ± 2·5
25	$HgCl_2$	,,	12·0 ± 1·0	0·06 ± 0·02	0·72 ± 0·30
,,	BF_3–Et_2O	$Ph{\cdot}NO_2$	24·0 ± 3·0	0·11 ± 0·04	2·64 ± 1·32
,,	BF_3–2AcOH	$(CH_2Cl)_2$	24·0 ± 2·0	0·08 ± 0·03	1·82 ± 0·84
,,	,,	C_6H_6	51·0 ± 15	0 ± 0·01	—
		CEVE (1) *and α-methylstyrene* (2)			
−30	BF_3–2AcOH	$(CH_2Cl)_2$	2·0 ± 0·2	0·75 ± 0·07	1·50 ± 0·3
0	,,	,,	3·9 ± 0·15	0·48 ± 0·04	1·87 ± 0·4
25	,,	,,	4·5 ± 0·5	0·07 ± 0·01	0·31 ± 0·08

DISCUSSION

The tabulated results show that in these copolymerisations 2-chloroethyl vinyl ether (CEVE) is much more reactive than styrene and appreciably more reactive than α-methylstyrene. With CEVE-styrene, the r-values vary widely with the experimental conditions. Values of $r_1 = 36$, $r_2 = 3$, recently reported by Kanoh *et al.*[5] for this system initiated by iodine in ethylene dichloride at 30° emphasise this variation.

Such effects of catalyst and solvent on the r-values have been observed with other

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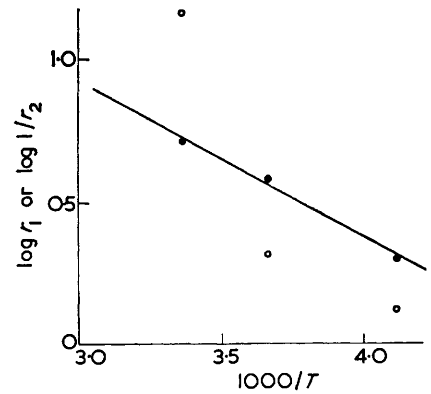
[3] Joshi and Kapur, *J. Polymer Sci.*, 1954, **14**, 508.

[4] Eley and Saunders, *J.*, 1954, 1677; Eley and Coombes, *J.*, 1957, 3700.

[5] Kanoh, Gotoh, Higashimura, and Okamura, *Makromol. Chem.*, 1963, **63**, 106.

monomer pairs,[6] but have tended to be disregarded as anomalies and associated with heterogeneity in the reaction systems.[7] Here the system initiated by fuller's earth was definitely heterogeneous and its results should be excluded from discussion. The other systems were homogeneous and believed comparable. The uncertainties in the r-values are large, it is true, though not abnormally so for a system where the monomers differ so greatly in reactivity, with consequent greater sensitivity of the final computed r-values to the experimental errors in determination of copolymer composition. However, the variations in r-values found with different catalysts and solvents are much greater than the experimental uncertainties. It seems fair to take this variation as confirmation of the recent evidence[8] from homopolymerisation that the reactivities in cationic propagation reactions are not absolute quantities but depend upon the nature of the counter-anion and the solvent.

In no case do the derived reactivity ratios give a product r_1r_2 equal to or very close to unity, as would be expected for " ideal copolymerisation." The uncertainty in the value of this product is, of course, larger than that in the separate values of r_1 and r_2, but as shown in the Table, even the extremes of the uncertainty of r_1r_2 include unity in only two cases. The best interpretation would seem to be that these results indicate varying, and in some cases considerable, departures from ideal copolymerisation. In cationic copolymerisation many systems have been found to be approximately ideal, but there have always been exceptions, recent examples being the copolymerisation of styrene and substituted styrenes by stannic and titanic chloride reported by Tobolski and Boudreau[9] With various styrene derivatives and CEVE, Kanoh *et al.*[5] have found extreme examples, with both r_1 and r_2 greater than unity and the product as high as 225 (4-methylstyrene–CEVE). Such behaviour, implying that both propagating species have strong preference for their own monomers, normally means that no true copolymer is formed, but only a mixture of the separate homopolymers.



Temperature-dependence of reactivity ratios in the copolymerisation of CEVE (1) with α-methylstyrene (2). ● $\log r_1$. ○ $\log 1/r_2$.

If the influence of the counter-anion (and solvent) is allowed for, it is possible to understand why a given pair of monomers may show ideal behaviour in some systems but not in others, and why even in ideal copolymerisation the apparent relative reactivities of the monomers may vary. Ideal behaviour ($r_1 = k_{11}/k_{12} = 1/r_2 = k_{21}/k_{22}$) will be observed when the reactivities of the propagating species are either unaffected,* or equally affected

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* The reactivities of the two propagating species need not be identical, as has been stated by many writers, including the present (D. C. P.). I am indebted to Dr. J. F. Henderson for this correction.

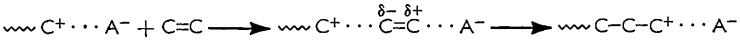
[6] Florin, *J. Amer. Chem. Soc.*, 1951, **73**, 4468.

[7] Pepper, *Quart. Rev.*, 1954, **8**, 118.

[8] Pepper and Reilly, *J. Polymer Sci.*, 1962, **58**, 639; Kanoh, Higashimura, and Okamura, *Chem. High Polymers, Japan*, 1962, **19**, 181; *Makromol. Chem.*, 1962, **56**, 65.

[9] Tobolski and Boudreau, *J. Polymer Sci.*, 1961, **51**, 857.

by the two monomers. Only in the former case will the ratio r_1 give a valid ratio of the reactivities of the two monomers. According to the nature of the catalyst anion and the solvating and other polar properties of the solvent, the propagating species in a cationic polymerisation may be expected to vary from effectively a free cation to a tightly bound ion-pair. In the latter case, the reaction has been represented[5] as:



$$\sim\!\sim C^{+}\cdots A^{-} + C{=}C \longrightarrow \sim\!\sim C^{+}\cdots \overset{\delta-}{C}{=}\overset{\delta+}{C}\cdots A^{-} \longrightarrow \sim\!\sim C{-}C{-}C^{+}\cdots A^{-}$$

With this type of mechanism the nature of the monomer will affect the reactivity of the propagating species, and the different monomers in a copolymerisation may do so differently (by virtue of their different size, geometry, or polarisibility), thus causing non-ideal copolymerisation.

The reactivity ratios in CEVE–α-methylstyrene copolymerisations show an appreciable temperature coefficient. The logarithm of r_1 is approximately linear with $1/T$ (see Figure), corresponding to a difference in activation energy for the two addition reactions to the CEVE cation, $E_{11} - E_{12} \gtrsim 2{\cdot}5$ kcal./mole. For addition to the α-methylstyrene carbonium ion, r_2 has a very low value (0·07) at 25° (though Dunphy and Marvell[10] find $r_2 = 0{\cdot}3$ with stannic chloride at 30°). This might be thought to be the result of depropagation since α-methylstyrene has its " ceiling temperature " in this region. However, at the lowest temperatures we should not expect depropagation to be important, and here we find that the temperature-dependence of $1/r_2$ is similar to that of r_1, *i.e.*, $E_{21} - E_{22}$ is also $\sim$2 kcal./mole.

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[*Received, January* 31*st*, 1963.]

[10] Dunphy and Marvell, *J. Polymer Sci.*, 1960, **47**, 1.