

Copolymerization of Methacrylic Acid Esters with Methacrylonitrile

G. G. CAMERON, D. H. GRANT, N. GRASSIE, J. E. LAMB, and I. C. McNEILL, *Chemistry Department, The University, Glasgow, W.2., Scotland*

The investigation of copolymerization reactions is probably the most productive and experimentally the easiest method of gaining information about the effect of structure on radical molecule reactions. A theoretical approach to reactivity in copolymerization reactions has recently been made using a molecular orbital treatment,¹ but the number of systems to which it has been applied is limited. A theoretical study by Evans, Gergely, and Seaman² has provided some foundation for the semiempirical Alfrey-Price $Q-e$ scheme³ which seeks to explain radical-molecule reactivity in terms of resonance stabilization (Q) and polarity (e) effects, and taking into account the variety of structures to which this scheme has been applied, it must be considered qualitatively satisfactory despite its limitations. A number of the apparent anomalies are qualitatively explicable as resulting from steric effects.³

Successive small changes in structure are represented by the homologous series of methacrylate esters, and it is of interest to discover whether the differences in reactivity which occur in the series can be explained in terms of these three factors.

Such investigations may also shed some light upon the relative behaviors of these monomers in homopolymerization and upon the depolymerization of the resulting homopolymers, both of which reactions involve the same kind of radicals.

The common comonomer, methacrylonitrile, was chosen partially because of the ease of analysis of the copolymers (nitrogen estimation) but principally because certain of the copolymers are of interest in degradation studies.⁴

EXPERIMENTAL

Monomers

Methyl, ethyl, *n*-butyl, and isobutyl methacrylates and methacrylic acid were supplied by I.C.I. Ltd., and styrene by Forth Chemicals Ltd. Hexyl, octyl, and stearyl methacrylates were gifted by the United States Rubber Company. *n*-Propyl,⁵ isopropyl,⁵ and *tert*-butyl⁶ methacrylates

were prepared by standard methods, and methacrylonitrile as previously described.⁷

Phenolic inhibitors were removed by washing with caustic soda solution except in the case of methacrylic acid. Monomers were then washed with distilled water, dried over calcium chloride, distilled under reduced pressure, and stored at -18°C . Methacrylic acid, which was stabilized by pyrogallol, was only distilled under reduced pressure.

Catalyst

Benzoyl peroxide, purified as previously described⁷ was used as catalyst. A 0.7% (w/v) solution was used, except in the preparation of methacrylic acid copolymers when 0.01% gave sufficiently high rates of polymerization.

Preparation of Copolymers

In the preparation of copolymers of methacrylonitrile with the more volatile monomers (styrene and methyl, ethyl, and the propyl and butyl methacrylates), both monomers were degassed and twice distilled under high vacuum, the second time from a calibrated reservoir into dilatometers of approximately 30 ml. capacity into which the catalyst had previously been introduced.

The less volatile monomers were measured directly into dilatometers from a burette and thoroughly degassed. Methacrylonitrile was introduced as in the foregoing and the dilatometers sealed off under vacuum.

All polymerizations were carried out at 80°C . to a maximum of 5% conversion. The copolymers were precipitated with methanol (ether for methacrylic acid copolymers), roughly dried, redissolved in acetone (dioxane for styrene copolymers and chloroform for stearyl methacrylate copolymers), and carefully reprecipitated as a powder. After filtration the copolymers were dried at 60°C . and ground for analysis.

Trapped solvents, which usually constituted 1–2% of the weight of the polymers (7% in methacrylic acid copolymers) were estimated by observing the decrease in weight of a sample heated to constant weight in vacuum at 160°C .⁸ and allowed for in the copolymer analysis. Under these conditions stearyl methacrylate copolymers showed a continuous loss in weight which must be attributed to degradation. The content of volatiles was assumed to be the same as that for the octyl ester copolymers.

Analysis of Copolymers

Copolymer composition was determined by nitrogen estimation using the Kjeldahl method. Some preliminary estimations on pure polymethacrylonitrile using copper sulfate as catalyst in the sulfuric acid digestion gave low nitrogen values (18.6% compared with the theoretical value of 20.9%). Using B.D.H. mercury catalyst and a maximum of 0.3 g. of polymer, however, values of $20.5 \pm 0.2\%$ were consistently obtained. This

TABLE I
 Monomer Mixture and Copolymer Molar Ratios (M_1)/(M_2)^a

Monomer mixture	Copolymer	Monomer mixture	Copolymer
$M_2 = \text{Styrene}$		$M_2 = \text{Isopropyl methacrylate}$	
7.50	2.96	10.57	5.32
9.98	3.13	7.70	3.64
1.07	0.980	0.252	0.233
1.46	1.105	0.254	0.236
0.296	0.449		
0.368	0.554	$M_2 = n\text{-Butyl methacrylate}$	
		0.221	0.247
$M_2 = \text{Methacrylic acid}$		0.316	0.362
4.675	2.69	1.958	1.54
2.160	1.29	2.438	1.77
1.515	0.94		
0.669	0.398	$M_2 = \text{Isobutyl methacrylate}$	
9.46	6.40	5.13	4.31
0.454	0.27	2.39	2.10
		0.570	0.654
$M_2 = \text{Methyl methacrylate}$		0.336	0.413
0.439	0.485		
1.51	1.38	$M_2 = \text{tert-Butyl methacrylate}$	
4.19	3.37	2.64	1.49
		1.78	1.23
$M_2 = \text{Ethyl methacrylate}$		0.620	0.594
1.525	1.085	0.463	0.453
0.392	0.375		
8.11	4.30	$M_2 = n\text{-Amyl methacrylate}$	
0.751	0.655	7.05	4.27
		5.52	3.89
$M_2 = n\text{-Propyl methacrylate}$		2.57	2.02
14.85	5.37	1.63	1.41
14.58	4.30	0.466	0.611
0.603	0.502	0.445	0.567
0.572	0.487		
		$M_2 = \text{Stearyl methacrylate}$	
$M_2 = n\text{-Hexyl methacrylate}$		26.1	23.2
11.43	8.77	9.59	9.05
2.86	2.58	4.25	3.76
0.571	0.764	1.65	1.48
0.578	0.698	1.45	1.32
2.38	2.35		
		$M_2 = n\text{-Octyl methacrylate}$	
		12.49	9.62
		12.42	9.76
		3.11	2.90
		2.70	2.50
		0.540	0.624
		0.708	0.827

^a $M_1 = \text{methacrylonitrile}$.

order of error will not affect significantly the reactivity ratio values, but in order to minimize the error, compositions of copolymers were calculated using 20.5% as the theoretical nitrogen content of methacrylonitrile. All estimations were carried out at least in duplicate, some in triplicate and were self-consistent within the limits of $\pm 0.08\%$.

RESULTS

Monomer mixture and the corresponding copolymer compositions are presented in Table I. Reactivity ratios were obtained by the intersection method and all lie within the limits ± 0.08 . Using styrene as standard, with $Q = 1.0$, $e = -0.8$, the Alfrey-Price Q and e values for methacrylonitrile were found to be 0.78 and 0.72, respectively. Taking these in turn, Q and e values for methacrylic acid and the various esters were calculated. These results are presented in Table II.

TABLE II
Reactivity Ratios and Q and e Values at 80°C.^a

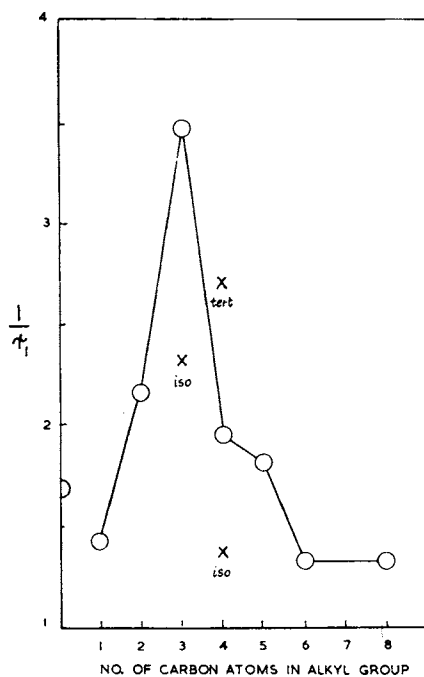
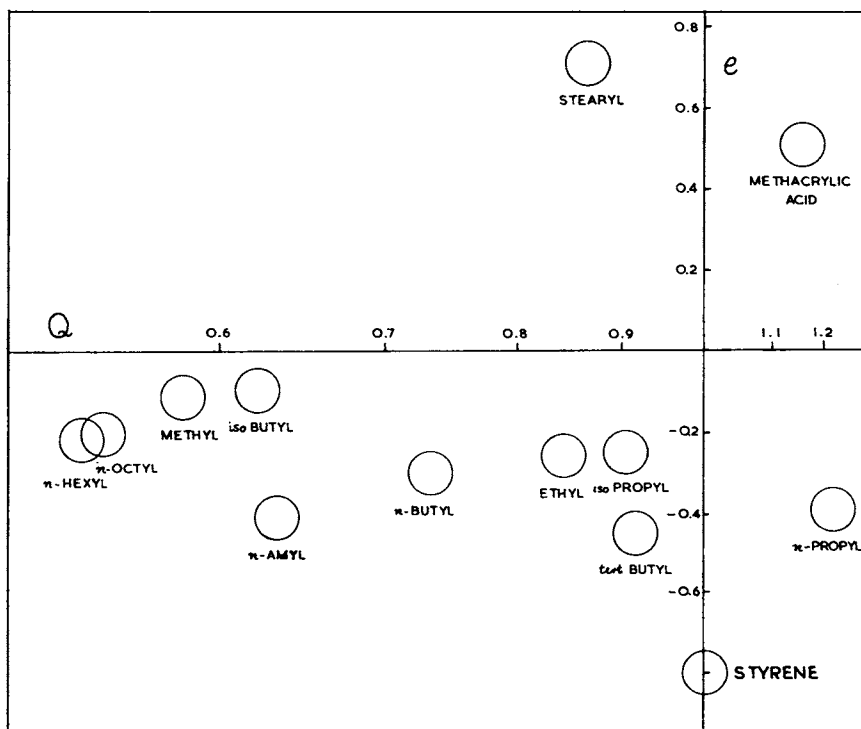
M_2	r_1	r_2	$r_1 r_2$	Q	e	$1/r_1$
Styrene	0.26	0.38	0.099	—	—	
Methacrylic acid	0.59	1.63	0.96	1.15	0.52	1.69
Methyl methacrylate	0.70	0.74	0.518	0.62	-0.09	1.43
Ethyl methacrylate	0.46	0.83	0.382	0.84	-0.25	2.17
<i>n</i> -Propyl methacrylate	0.29	0.79	0.229	1.21	-0.39	3.46
Isopropyl methacrylate	0.43	0.92	0.396	0.90	-0.24	2.32
<i>n</i> -Butyl methacrylate	0.51	0.69	0.352	0.73	-0.30	1.96
Isobutyl methacrylate	0.73	0.67	0.49	0.58	-0.12	1.37
<i>tert</i> -Butyl methacrylate	0.37	0.70	0.259	0.91	-0.44	2.70
<i>n</i> -Amyl methacrylate	0.55	0.51	0.28	0.63	-0.41	1.82
<i>n</i> -Hexyl methacrylate	0.75	0.56	0.42	0.53	-0.21	1.33
<i>n</i> -Octyl methacrylate	0.75	0.58	0.435	0.54	-0.20	1.33
Stearyl methacrylate	0.90	1.13	1.00	0.87	0.72	1.11

^a M_1 = methacrylonitrile

For the styrene/methacrylonitrile system reactivity ratio values $r_1 = 0.16 \pm 0.06$, $r_2 = 0.30 \pm 0.10$ (60°C.) and $r_1 = 0.25 \pm 0.02$, $r_2 = 0.25 \pm 0.02$ (80°C.) have previously been obtained^{9,10} while for methacrylonitrile/methyl methacrylate the values $r_1 = 0.65 \pm 0.06$, $r_2 = 0.67 \pm 0.10$ (60°C.) have been reported.⁹ The values in Table I are in reasonable agreement with these.

DISCUSSION

The relative reactivities toward the methacrylonitrile radical of the various comonomers are measured by the corresponding $1/r_1$ values. The effect of the length of the ester side-chain on this reactivity is demonstrated in Figure 1. Among the normal esters the reactivity increases markedly on passing from methyl to propyl, thereafter decreasing to a fairly constant value at hexyl.

Fig. 1. Effect of size of alkyl group on $1/r_1$.Fig. 2. Q - e map.

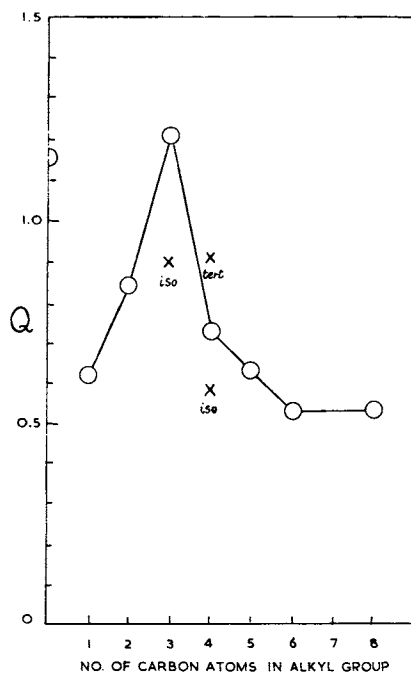
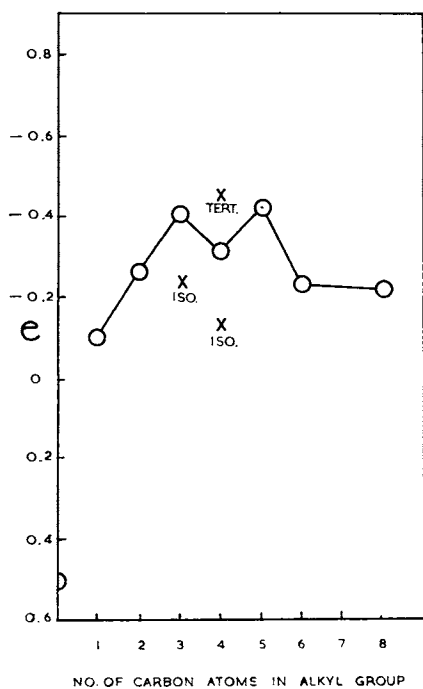
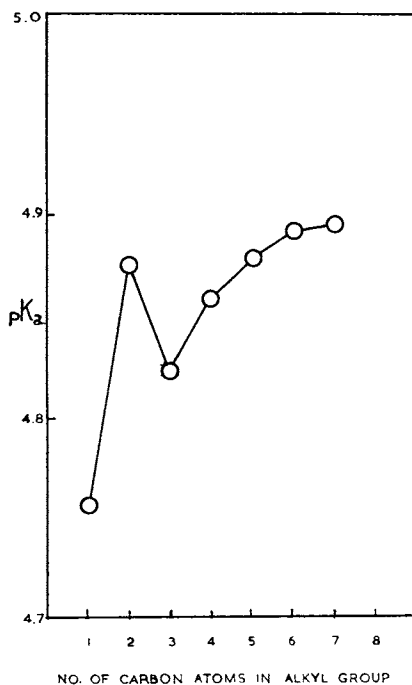
Fig. 3. Effect of size of alkyl group on Q .Fig. 4. Effect of size of alkyl group on e .

Fig. 5. Effect of alkyl chain length on the strength of normal fatty acids.

The Alfrey-Price Q and e values are plotted on a Q - e map in Figure 2, and their variation with alkyl chain length in Figures 3 and 4. The Q values follow the same pattern as the relative reactivities showing that they are principally responsible for determining monomer reactivity in these systems, polar influences exerting a relatively minor effect.

Results for stearyl methacrylate are not easily accounted for on the basis of the discussion which follows. In view of the instability exhibited by stearyl methacrylate copolymers during the estimation of volatiles, it seems possible that the copolymer composition may be modified by degradation processes occurring during copolymerization.¹¹ This system is not therefore included in Figures 1, 3, or 4 or in this discussion. Methacrylic acid is also omitted since different influences are involved in its resonance stabilization and polarity factors which makes it difficult to compare directly with the esters.

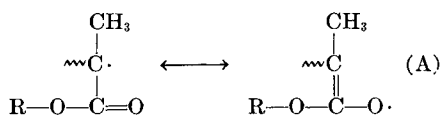
In the Alfrey-Price scheme, the Q values are a measure of the effect of substituents on the general reactivity of the monomer. In general substitution stabilizes both the monomer and the radical resulting from its addition to a growing polymer chain but the latter to a very much greater extent. Evans has his co-workers,² in their theoretical study, relate the specific reactivity of the monomer Q to the conjugation energies of the monomer C_M and the radical, C_F , by

$$Q = \exp\{\alpha(C_F - C_M)/RT\}$$

in which α is a constant. The reactivity of the monomer is therefore determined almost entirely by the stability of the resulting radical, and the variation in the Q values of the monomer series under discussion must be interpreted primarily in terms of the stabilizing effect of the changing substituent.

The electron donating power of n -alkyl groups increases with the length of the alkyl chain, rapidly at first but reaching a maximum about hexyl and remaining fairly constant thereafter. Thus increasing the length of the alkyl chain in the fatty acids results in a decrease in acid strength to a limiting value as shown in Figure 5.¹² The discontinuity at butyl has been explained in terms of interaction between the carboxyl group and the terminal methyl group of the alkyl chain.

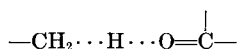
The principal structures contributing to radical stabilization are



On passing from methyl, through ethyl to propyl methacrylate the increasing Q values can be explained in terms of greater electron release increasing radical stabilization through contributions from such forms as



Molecular models indicate that the butyl group is the shortest in which the terminal methyl group can approach closely to the carbonyl group of the same ester unit. Any interaction between these two parts of the molecule,



would decrease the resonance stabilization contribution of the radical form (A) by rendering withdrawal of electrons from the oxygen atom more difficult.

Direct steric inhibition of resonance may also play a part in decreasing the stability of the higher methacrylate radicals since these large groups can only be accommodated as a result of considerable distortion of the molecular structure, and any rotation about the carbon-carbon bond joining the side-chain to the main polymer chain will result in the carbonyl group being forced out of the plane of the rest of the resonating system.

Electron release in the series methyl, ethyl, isopropyl, and *tert*-butyl should increase in that order and this is indeed reflected in the *Q* values. The increases on passing from ethyl to isopropyl and to *tert*-butyl might be expected to be rather larger but they may be restricted by the steric effect of the increasing size of the group. The value for isobutyl methacrylate is also rather lower than might have been expected on the basis of electron release only.

Polar interaction of radical and monomer, as measured by the *e* value in the *Q-e* scheme, is found to be of relatively minor importance in these copolymerizations. The small variations as the alkyl group increases in size are mostly in the direction expected. The *e* values for the methyl, ethyl and *n*-propyl esters show an increase in the negative sense which accords with the effect of increased electron release. The value for the butyl ester is rather lower than would be expected, although the relative differences between the values for propyl, butyl, and amyl may be at the limits of experimental error. After amyl there is a further fall in *e* at hexyl and octyl. Molecular models show that the hexyl group is the smallest necessary for significant direct steric interference with the radical itself, and it is suggested that this decrease in *e* is the result of the screening effect of the side-chain. Among the branched chain esters, isopropyl and *tert*-butyl have reasonable *e* values but that for iso-butyl is distinctly lower than expected.

Crawford has made a rough assessment of the degradability to monomer of a series of alkyl methacrylates.⁵ Extent of degradation in a fixed time under standard conditions was used as a measure of ease of degradation. By plotting these extents of degradation against alkyl chain length, he obtained a relationship very similar to that in Figure 2 although the maximum occurs at butyl methacrylate. These results are not strictly comparable since the degradability measured in this way must depend upon a number of factors. Not the least of these will be the initiation process, however, which consists of scission of the polymer chain to form radicals.

The ease of initiation will be strongly associated with the resonance stabilization of these radicals which are identical with those occurring in copolymerization. A quantitative comparison with copolymerization will only be possible, however, when the separate rate constants governing the depolymerization reaction have been measured for a variety of monomers.

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Synopsis

The reactivity ratios in the copolymerization of methacrylonitrile with styrene, methacrylic acid, and eleven alkyl methacrylates have been determined and the Alfrey-Price Q and e values calculated. Monomer reactivity in these systems is principally a function of resonance stabilization (Q), polar factors (e) playing a relatively minor role. With the exception of the stearyl ester, the changes in the Q and e values which occur on ascending the homologous series can be accounted for qualitatively in terms of the expected relative electronic displacements and of the steric effects caused by the various alkyl groups. Some correlation between monomer reactivity and the depolymerizability of the corresponding polymer has been noted.

Résumé

On a déterminé les rapports de réactivité en cours de copolymérisation du nitrile-méthacrylique avec le styrène, l'acide méthacrylique et onze méthacrylates d'alcoyles. On a calculé les valeurs Q et e de l'équation d'Alfrey-Price. La réactivité du monomère dans ces systèmes apparaît surtout comme une fonction de l'énergie de résonance de stabilisation (Q); les facteurs polaires (e) jouant un rôle plutôt moindre. Si l'on en excepte l'ester de stéaryle, les changements dans les valeurs de Q et de e , qui se présentent en parcourant la série homologue, peuvent être justifiés qualitativement par le déplacement relatif d'électrons de des effets stériques causés par les divers groupes alcoyles. On a également noté une corrélation entre la réactivité du monomère et la possibilité de dépolymérisation du polymère correspondant.

Zusammenfassung

Die Reaktionsfähigkeits-verhältnisse bei der Copolymerisation von Methacrylnitril mit Styrol, Methacrylsäure und elf Alkylmethacrylaten wurden bestimmt und die Q - und e Werte nach Alfrey-Price berechnet. Die Reaktionsfähigkeit des Monomeren ist in diesen Systemen hauptsächlich eine Funktion des Resonanz-stabilisierung (Q), während polare Faktoren (e) eine verhältnismässig geringere Rolle spielen. Mit Ausnahme der Stearylester, können die Änderungen der Q - und e -Werte, die beim Fortschreiten in der homologen Reihe auftreten, qualitativ auf Grund der erwarteten, relativen Elektronenverschiebungen und der durch die verschiedenen Alkylgruppen verursachten sterischen Effekte erklärt werden. Eine gewisse Beziehung zwischen der Reaktionsfähigkeit der Monomeren und der Neigung der entsprechenden Polymeren zur Depolymerisation wurde festgestellt.

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