

Polymerization

Radical Copolymerization of 2-Hydroxyethylacrylate with Alkylacrylate Determination of the Reactivity Ratios

J.M. Catala*, A. Nonn, J.M. Pujol, and J. Brossas*

Institut Charles Sadron, CRM-EAHP, CNRS-ULP, 6, rue Boussingault,
F-67083 Strasbourg Cedex, France

Summary

The copolymerization of hydroxyethylacrylate with methyl-ethyl- and butyl-acrylate was studied at 60°C using azo-bis-isobutyronitrile as the initiator. The monomer reactivity ratios were determined by the Fineman method. The results show that the methylacrylate-hydroxyethylacrylate monomers copolymerize in a completely random manner (Bernouillian behaviour). For the other monomer pairs, an increase in the chain length of the alkyl ester group favours the addition of hydroxyethylacrylate monomer to the alkylacrylate polymer radicals.

Introduction

The copolymerization of methacrylic or acrylic esters with hydroxyethylmethacrylate has been the subject of much interest because of the applications (1) of these polymers as coatings, adhesives and hydrogels. Curiously, no work has been done in homogeneous phase with hydroxyethylacrylate. Nevertheless, this monomer copolymerizes with alkylacrylate to give a low glass transition temperature copolymers even for high contents of hydroxy groups. For this reason, after crosslinking by a diisocyanate, the resulting networks show elastomeric properties at low temperatures. However, the properties of such networks can be affected by the distribution of the hydroxyle groups along the chain. In order to define the sequence-length distribution of the two monomers, it was necessary to determine the reactivity ratios. In this paper we present a study of the copolymerization of hydroxyethylacrylate monomer (HEA) with methylacrylate (MA), ethylacrylate (EA) and butylacrylate (BA).

Experimental

Methylacrylate, ethylacrylate, n.butylacrylate

The monomer were distilled under reduced pressure and stored under argon before use.

Hydroxyethylacrylate

This monomer as received (Fluka) contained 25% impurities. It was purified as follows:

* To whom offprint requests should be sent

. after dissolution of the monomer in water (1/4), hydroquinone (0.1%) was added to prevent polymerization. The non-functional impurities ($\text{CH}_2=\text{CH}-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CO}-\text{CH}=\text{CH}_2$) were extracted by repeated washings with hexane (10 times). The aqueous solution was salted (250 g/l) and the monomer removed by ether extraction (4 times). After the addition of hydroquinone and drying on CaSO_4 , the ether solution was evaporated and the monomer kept over molecular sieves (4 Å). The monomer was distilled just before use under reduced pressure and after the addition of Na_2CO_3 (0.2%) and polypropylene glycol (3%). The purity of the monomer was tested with VPC.

Azo-bis-isobutyronitrile

AIBN was recrystallized in methanol and dried under vacuum.

Polymerization

The copolymerization was carried out under argon in 2-ethoxyethanol for methylacrylate and 2-methoxyethanol for the ethyl- and butylacrylate. After the addition of 0.2% of AIBN, the flask was kept at 60°C. At different times, one milliliter of the solution was taken out and cooled to -78°C, after addition of hydroquinone. Monomer concentrations of each sample were determined by vapor phase chromatography. An internal standard (decane) present in the reaction medium was used to normalize the injections. The chromatographic apparatus (Varian) was equipped with a flame ionization detection.

Different columns were used:

- . HEA - MA : filled column (2 m) with OV 17 at 20% on G 100-120 mesh chromosorb,
- . HEA - EA : SE 52 capillary column (20 m),
- . HEA - BA : OV 1 capillary column (10 m),

Results and discussion

The reactivity ratios r_1 , r_2 are related to the copolymer composition (F_1 , F_2) and the monomer feed composition (f_1 , f_2) by the general equations:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + r_2 f_2^2 + 2 f_1 f_2} \quad f_1 = \frac{[M_1]}{[M_1] + [M_2]} \quad f_2 = 1 - f_1$$

$$F_1 = \frac{d[M_1]}{d[M_1] + d[M_2]} \quad F_2 = 1 - F_1$$

The monomer concentration was determined by the injection of the monomer feed in VPC at different times. From the plots $[M_1] = f(t)$ and $[M_2] = f(t)$, the instantaneous composition of the copolymer is given by the slopes: $d[M_1] dt$ and $d[M_2] dt$.

In the case of HEA-MA copolymerization, we have observed that the monomer feed composition remains constant during the reaction. In fig. 1 we have shown the copolymer composition in HEA units (F_1) in relation to the mole fraction HEA in comonomer feed (f_1). It is apparent that the copolymer formed presents the same composition as the monomer feed.

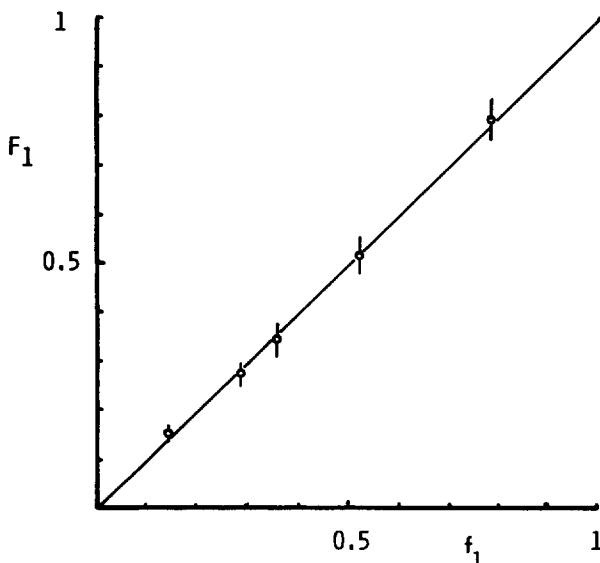


FIG. 1 - DEPENDENCE OF THE INSTANTANEOUS COPOLYMER COMPOSITION F_1 ON THE COMONOMER FEED COMPOSITION f_1 FOR HEA AND MA COMONOMERS

By the Fineman-Ross (2) method, we have evaluated the reactivity ratios as:

$$r_1(\text{HEA}) = r_2(\text{MA}) = 1.0 \pm 0.1$$

These results show that the polymer radicals have the same reactivity with either monomer ($k_{11} = k_{12}$, $k_{22} = k_{21}$). This behaviour is unusual in radical copolymerization because radical polymer reactivity and monomer reactivity depend on the opposite effects of the substituent (3); a substituent that increases monomer reactivity does so because it stabilizes and decreases the reactivity of the corresponding radical. In the case of hydroxyethylmethacrylate and alkylacrylate (4) the methyl group increases the reactivity of the HEMA monomer towards the polymer radicals, and the resulting copolymer shows a higher HEMA composition fraction than that of the monomer feed.

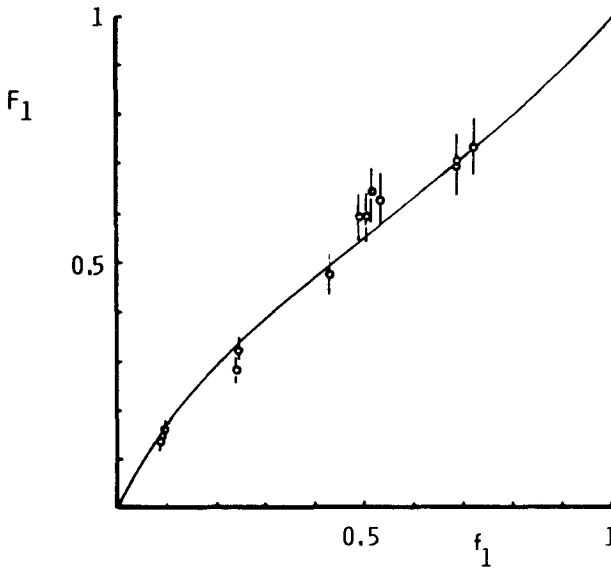


FIG. 2 - DEPENDENCE OF THE INSTANTANEOUS COPOLYMER COMPOSITION F_1 ON THE COMONOMER FEED COMPOSITION f_1 FOR HEA AND EA COMONOMERS

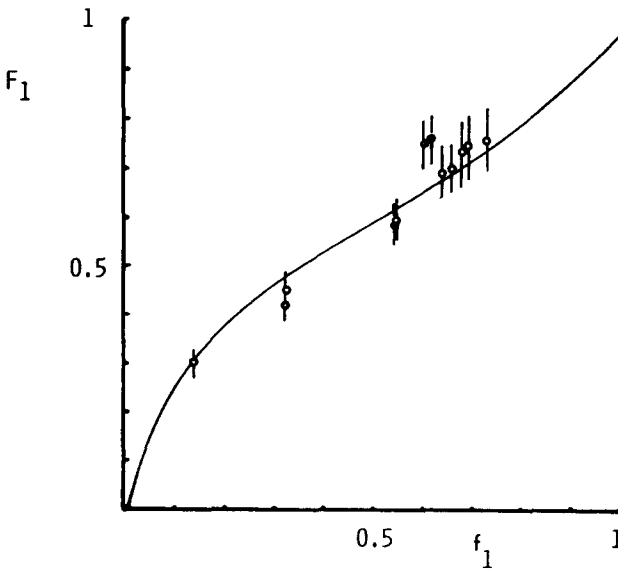


FIG. 3 - DEPENDENCE OF THE INSTANTANEOUS COPOLYMER COMPOSITION F_1 ON THE COMONOMER FEED COMPOSITION f_1 FOR HEA AND BA COMONOMERS

In our study all the monomers are acrylates, differing in their ester groups. As the inductive effect of such groups can be neglected, only steric effects may influence their reactivities. In the HEA-MA copolymerization, this effect is not observed and the copolymer shows a random placement of the two monomers along the chain (Bernouillian behaviour). In the other case, we observed (fig.2) that the copolymerization of HEA and EA produced a copolymer containing a greater HEA content than the monomer feed. This phenomenon is more pronounced for the HEA-BA copolymer (fig. 3). The corresponding reactivity ratios are collected in table 1:

Table 1 - Monomer reactivity ratios of HEA with methyl-, ethyl- and n.butylacrylates

Monomers	r_1	r_2
HEA-MA	1.00 ± 0.10	1.00 ± 0.10
HEA-EA	0.88 ± 0.09	0.50 ± 0.05
HEA-BA	0.94 ± 0.10	0.23 ± 0.03

Using this data, the reactivities of the different monomers towards the HEA polymer radical can be compared. The inverse of the reactivity ratios $1/r_1 = k_{12}/k_{11}$ gives the order of magnitude of the reactivity of the alkylacrylate monomers towards the same reference polymer radical. In our case, $1/r_1$ (table 1) remains practically constant (within experimental error). From this we conclude that the chain length of the ester groups has a negligible effects on the collision factor, and at least on the reactivity of the three acrylate monomers herein considered towards the HEA polymer radical.

From the r_2 values, we observe that an increase in the size of the ester group favours the introduction of the HEA monomer into the copolymer.

In conclusion, copolymers with pendent hydroxyle groups and low glass transition temperatures can be obtained from alkylacrylates and hydroxyethylacrylate. The hydroxyle content is generally higher than the monomer feed composition except for the methylacrylate which copolymerizes in a random manner for the whole monomer feed composition.

References

- 1) R.H. Yocum, E.B. Nyquist "Functional Monomers", Vol.1, Dekker, New-York (1973), p.328
- 2) M. Fineman, S.D.Ross, J.Polym.Sci. 5, 2 (1950)
- 3) G. Odian, "Principles of Polymerization" 2nd Ed.Wiley Int. Publications, New-York (1981)
- 4) I.K. Varma, S. Patnaik, Europ.Polym.J. 12, 259 (1975).