High conversion copolymerization of furfuryl methacrylate and *N*-vinylpyrrolidone. A kinetic approach to Skeist's treatment for free radical copolymerization in different reaction media

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The influence of reaction conditions and temperature on the free radical copolymerization of furfuryl methacrylate with *N*-vinylpyrrolidone, initiated by 2,2'-azobisisobutyronitrile (AIBN) is studied. The initiation step is promoted by the thermal decomposition at 50°C of the AIBN molecules in *N*,*N*-dimethylformamide (DMF) solution or photochemically at 0 and 40°C in bulk. The variation of the average composition of copolymer chains with the conversion for two different compositions of the monomer feed, $f_F^0 = 0.02$ and 0.50, is analysed from the classical integrated copolymerization equation. Since the reactivity ratios of this pair are very different, $r_F = 3.92$ and $r_P = 0.004$, a simplified approximation of the integrated Skeist's equation is proposed. The experimental data obtained under different experimental conditions fit adequately the theoretical predictions, suggesting that the reaction medium (solution or bulk) or initiation technique (thermal or photochemical) do not affect the average composition of the copolymer chains at different conversions. However, the variation of the cumulative composition of copolymer chains with the degree of conversion is very sensitive to the initial composition of monomer feed. In addition, the average rate of copolymerization seems to be also dependent on the feed composition.

(Keywords: copolymerization; furfuryl methacrylate; *N*-vinylpyrrolidone)

INTRODUCTION

The mechanism of the free radical copolymerization of vinyl and acrylic monomers traditionally has been considered to be little influenced by the initiation step[1,2], and the copolymerization scheme of the classical terminal model suggested by Mayo and Lewis[3] considers the variation of the composition of the reaction medium as well as that of the copolymer chains, according to four individual addition processes that correspond to the homopolymerization of both monomers *i–i* and *j–j* and the cross-propagation *i–j* and *j–i* additions[4].

On the other hand, the change of the composition of the reaction medium with conversion has a decisive influence on the characteristic microstructure and properties of the corresponding copolymers when the reactivity ratios r_i and r_j are very different. Only in the case of azeotropic copolymerization (at the azeotropic composition) or for ideal systems, does the composition of the reaction medium remain constant with conversion and therefore, the sequences of monomeric units along the copolymer chains are strictly homogeneous[5].

Recently[6] we have studied the free radical copolymerization in solution of furfuryl methacrylate (F) and *N*-vinylpyrrolidone (P) at low conversion (<5%) in order to know the corresponding kinetic parameters of the free radical copolymerization and the statistical distribution of monomeric sequences along the copolymer chains. The great difference of their reactivity ratios, $r_F = 3.92$ and $r_P = 0.004$, provides an excellent opportunity to study experimentally the influence of the initiation technique and reaction conditions on the kinetic parameters of copolymerization, and profit by the opportunity to study the copolymerization process using 2,2'-azobisisobutyronitrile (AIBN) as initiator but different techniques and temperatures to generate the free radical initiating species. The ability of promoting the homolytic breaking of the —N=N— azo bonds of AIBN molecules photochemically by the application of irradiation of the appropriate wavelength[7], allows this azo compound also to be employed as a photoinitiator which permits the study of the influence of temperature over a wide range of values both below and above room temperature.

In addition, the influence of conversion of both the feed composition and the cumulative composition of copolymer chains in terms of the molar fraction of F is

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studied following the treatment suggested by Skeist[8–11]. Considering the great difference in the reactivity ratios of F and P a simplification of the integrated copolymerization equation is proposed.

EXPERIMENTAL

Monomer preparation and purification of materials

F was prepared by transesterification of methyl methacrylate with furfuryl alcohol in the presence of sodium carbonate as catalyst and ionol as inhibitor. The product was distilled, dissolved in chloroform and passed through a chromatographic column containing Silica Gel 60 (Macherey-Nagel, Germany). The eluent was analysed by t.l.c. using Kieselgel 60 F 254 (Merck) as the stationary phase. The selected fraction was rotoevaporated in order to separate the solvent and then distilled. P (Fluka) was distilled under reduced pressure and used without further purification. AIBN (melting point 104°C) was purified by fractional crystallization from methanol and stored in the dark at low temperature. *N*,*N*-dimethylformamide (DMF) was dried over anhydrous magnesium sulfate for 2 days and later with phosphoric anhydride overnight. After drying, DMF was distilled under reduced pressure of nitrogen. Other reagents were of extra-pure grade and used as purchased.

Copolymerization

Copolymerization reactions were performed in DMF solution at 50 ± 0.1°C, in Pyrex glass ampoules sealed off under high vacuum. Monomer and initiator concentrations were 1.0 and 1.5×10^{-2} mol l^{-1}, respectively. The sealed ampoules were shaken vigorously and immersed in a water bath held at the required polymerization temperature. After the chosen reaction time, the ampoules were removed from the bath and at once the content was poured into a large excess of diethyl ether. The precipitated samples were washed with the precipitant mixture and dried under vacuum until constant weight was attained.

Copolymerization reactions photochemically initiated were carried out by direct irradiation of the sample placed in the holder sample of a differential scanning photocalorimeter. A standard Perkin–Elmer DSC-4 calorimeter was modified and adapted for measuring the polymerization rates of irradiated samples. The two ends of a two-branch u.v. light conducting fibre were inserted on the cover of the DSC-4 aluminium block by drilling holes directly above the sample and reference holders. The two-branch flexible u.v. light guides are terminated with a ferrule connector. As such, the input fibre is plugged into the side of an aluminium cylinder assembly, containing a manual shutter, to block the incident light on the input end of the light guide, an interference 365 nm filter (International Light NB-365), a solid i.r. filter (Schott KG-1) and neutral density filters. This assembly was mounted onto the water-cooled housing of a Hanovia Uvitron irradiation system provided with quartz lens and a 100 W high-pressure mercury lamp. The intensity of the transmitted light is controlled by adjusting the position of the internal cavity within the cylinder. With this arrangement it is possible to irradiate samples and monitor exotherm rates by d.s.c. simultaneously. For irradiation under anaerobic conditions, a standard nitrogen flow of 20 cm^3 min^{-1} was maintained in the d.s.c. chamber for at least 10 min before starting the irradiation. This time delay allows the oxygen dissolved in the sample to diffuse out and also ensures that the samples have attained the selected equilibrium temperature.

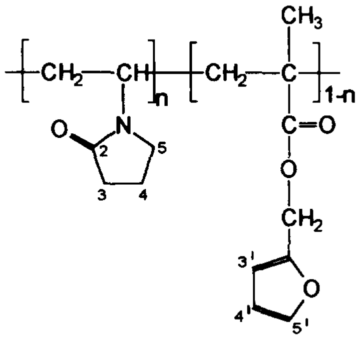
The d.s.c. calibration, data processing, incident light intensity determination, as well as complementary details, were performed as described elsewhere[12,13]. All polymerizations were carried out in bulk. The AIBN photoinitiator concentrations used in each case ensured total light absorption at 365 nm. Sample quantities of 20 μl were accurately measured using a Hamilton 25 μl syringe.

The above described photocalorimeter allows the preparation of copolymers at a selected temperature and with the required conversion.

Polymer characterization

The copolymers obtained from different mixtures of F and P were analysed by ^1H n.m.r. spectroscopy with a Varian XL-300 spectrometer working at 300 MHz. The spectra were recorded at 40°C using 5% (w/v) deuterated chloroform solutions.

The molar fraction of monomer units incorporated in the copolymer was determined from the ^1H n.m.r. spectra of copolymer samples prepared with different monomer compositions in the feed. The analysis was performed by comparing the integrated intensities of resonance signals with chemical shifts of 6.36 δ assigned to the protons in positions 3′ and 4′ of the aromatic furfuryl ring and 3.10 δ assigned to the protons in position 5 of the pyrrolidone ring (*Figure 1*):



RESULTS AND DISCUSSION

The kinetic parameters for the free radical copolymerization at low conversion (<5 wt%) of F and P in DMF solution over a wide composition interval of F in the monomer feed were determined using the method described in a previous work[6]. Copolymer samples prepared with different composition of the monomer feed from a very rich vinylpyrrolidone medium (98 mol%) to an equimolar monomers mixture, were isolated as indicated in the Experimental section, and analysed by ^1H n.m.r. spectroscopy. *Figure 1* shows the n.m.r. spectra of copolymers prepared with three different compositions, i.e. $F_F = 0.72, 0.64$ and 0.53. The average molar composition of the copolymer chains was determined by the comparison of the integrated intensities of the signals centred at 6.36 or 7.40 δ and 3.10 δ assigned to the hydrogen atoms of the functional groups indicated in the chemical structure of the repeating units shown above.

Figure 2 shows the average composition diagram obtained at low conversion (<5 wt%) as well as that

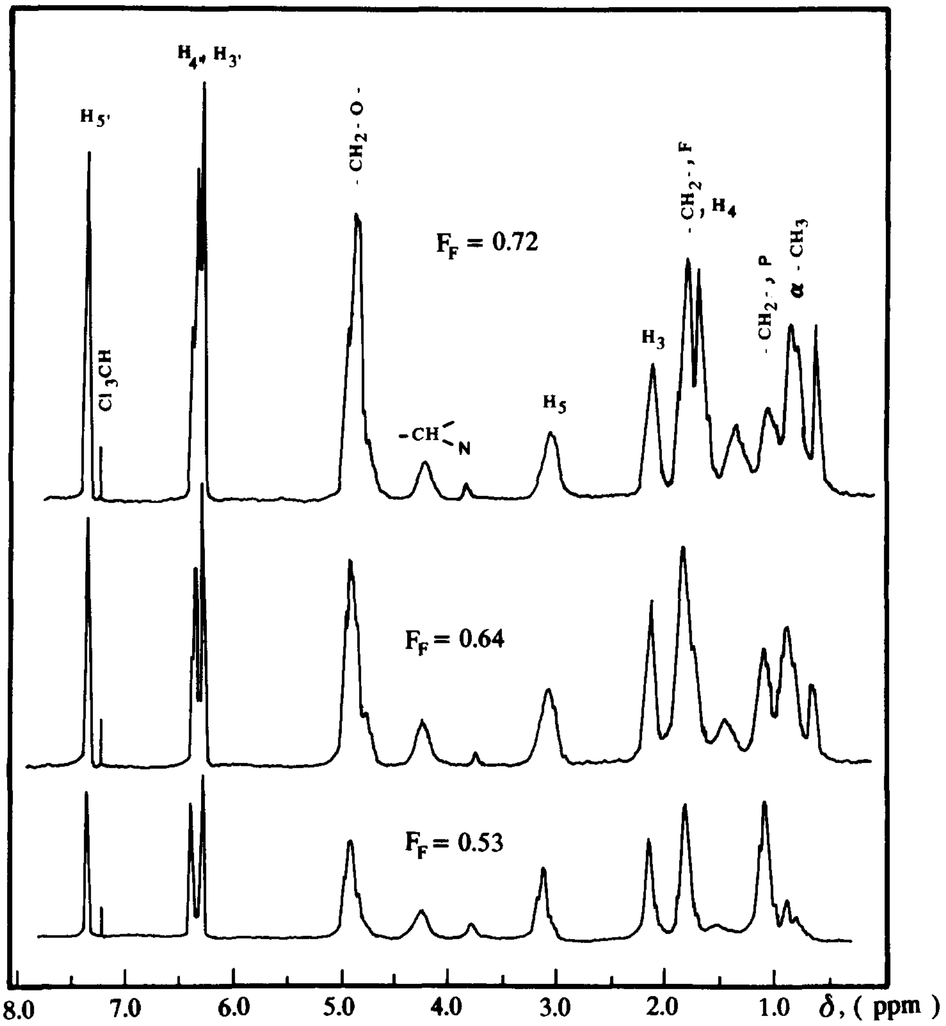


Figure 1 ^{1}H n.m.r. (300 MHz) spectra of F–P copolymers with different compositions. F_F is the molar fraction of furfuryl methacrylate in the copolymer chains

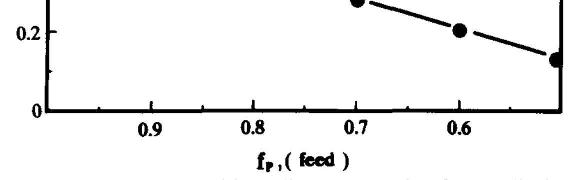


Figure 2 Average composition diagram of the free radical copolymerization of F with P in DMF solution at 50°C: (●) copolymers prepared at low conversion (<5 wt%); (◇) copolymers prepared at high conversion (>80 wt%); (– – –) diagram of an ideal copolymerization system or that of a random process at total conversion (100%)

obtained for copolymers prepared at high conversion, after a reaction time of 30 h. The solid symbols correspond to the experimental composition data obtained at low conversion, whereas the solid curve represents the composition expected according to the classical model of Mayo and Lewis[3,14]. It is apparent that the diagram obtained deviates noticeably from the ideal behaviour that is represented by the straight dashed line in *Figure 2*, and at low conversions very righ F copolymers are obtained, even for feed compositions with a concentration of P as high as 98 mol%. From these data the values of r_F and r_P were determined by different methods[15] and the most probable values turned out to be $r_F = 3.92$ and $r_P = 0.004$. This means that the reactivity of F-ending free growing macroradicals towards P monomer is 0.24 times that of F monomer, but the reactivity of P-ending free growing macroradicals towards F monomer is 250 times that of P monomer. Therefore, it can be expected that isolated P monomeric units may be distributed in long sequences of F units, at least for conversions of <10%.

For copolymers prepared at total conversion it would be expected that the average molar composition should be the same as the initial monomer feed, according to the classical free radical mechanism of polymerization. However, in the experimental conditions used for the preparation of these copolymers it is not possible to reach total conversion (100%), even with very long reaction times. In fact, a conversion of ~85 wt% is reached after 16 h of reaction, but this value is not increased for reaction times of 24 or even 48 h. This behaviour was explained by taking into consideration the relatively low reactivity of P and the so-called kinetic model of dead-end polymerization described by Tobolski *et al.*[16]. According to this model, when a free radical polymerization is initiated by a peroxide or azo compound like AIBN, the concentration of free radicals generated in the reaction medium at a given temperature does not remain constant for a long reaction time. It is necessary to consider that the deactivation of free radicals is produced by ineffective collisions even with the wall of the reactor and/or by participation in termination reactions. This is a random process that can be expressed mathematically by the well-known exponential decay function:

$$[I]=[I]_0 e^{-k_d t} \qquad (1)$$

where $[I]$ is the initiator concentration, $[I]_0$ is the initial initiator concentration, k_d is the decay constant and t is time.

In this way, $[I]$ decreases exponentially and therefore, when the reaction time is long, a limiting conversion is reached. This has an important effect on the average composition of the copolymers prepared at high conversion, as shown in *Figure 2*. If a total conversion (100%) would have been reached, the composition of copolymers would have fitted the straight broken line representing the ideal behaviour. However, the open symbols deviate from the ideal behaviour, with the composition of copolymers decreasing linearly as the molar fraction of P in the feed decreases. This result can be easily explained as a first approximation if we take into account that the 15 wt% of non-polymerized monomer corresponds almost exclusively to P because of its poor reactivity with respect to F towards both kinds of growing free radicals. However, the content of P in the copolymers prepared at high conversion is noticeably higher than that of copolymers prepared at low conversion from the same composition of the feed, which gives the idea of the presence of long P sequences for copolymers prepared in a feed very rich in P. This fact implies important consequences on the properties of these systems, as for example the solubility and swelling behaviour of films prepared with these copolymers[17].

The enormous difference in the reactivity of these monomers and radicals in the copolymerization reaction, provides an excellent system to study the effect of conversion on the composition and distribution of monomeric units along the copolymer chains, which on the other hand is of practical interest since for most applications, copolymers at conversions as high as possible should be obtained.

Also this system offers a good opportunity to study comparatively the effect of the polymerization technique on the composition of copolymer chains, and therefore, in this paper we present data of the composition of copolymers prepared using two different initiation techniques, i.e. thermal and photochemical decomposition of AIBN at several temperatures, as well as two different polymerization media, bulk for the photochemically initiated experiments and solution with a total concentration of monomers of 1 mol l^{-1} for thermally induced copolymerization reactions. In order to compare the experimental data with the prediction according to the classical kinetic scheme of the copolymerization process we have considered the treatment initially suggested by Skeist[8].

Meyer and Lowry[18] have shown that Skeist's equation:

$$\ln\left(\frac{M}{M_0}\right)=\int_{f_1^0}^{f_1}\frac{\mathrm{d}f_1}{F_1-f_1} \qquad (2)$$

where M and M_0 represent the total numbers of moles present in the monomer feed at a given time t and at time 0, respectively, can be readily integrated provided that F_1, the instantaneous copolymer composition, is expressed in terms of f_1, the corresponding instantaneous monomer composition, and the monomer reactivity ratios by means of the Mayo–Lewis[3] instantaneous copolymer composition equation. For $r_1 \neq 1$ and $r_2 \neq 1$ they obtained:

$$\frac{M}{M_0}=\left(\frac{f_1}{f_1^0}\right)^{\alpha}\left(\frac{f_2}{f_2^0}\right)^{\beta}\left(\frac{f_1^0-\delta}{f_1-\delta}\right)^{\gamma} \qquad (3)$$

where $\alpha=r_2/(1-r_2)$, $\beta=r_1/(1-r_1)$, $\gamma=(1-r_1r_2)/(1-r_1)(1-r_2)$ and $\delta=(1-r_2)/(2-r_1-r_2)$.

For systems such as the one under study, for which $r_1>1$ and $r_2 \ll 1$ the constants α, β, γ and δ in equation (3) can be reduced to a', β', γ' and δ', respectively, where $\alpha'=r_2$, $\beta'=r_1/(1-r_1)$, $\gamma'=1/(1-r_1)$ and $\delta'=1/(2-r_1)$. We have found that the error introduced in M/M_0 by such simplifying substitution is of the order of 0.1% for the system studied in this work. This also can be applied to other systems with the condition that $r_i \gg r_j$ $(i, j=1, 2)$.

From a simple mass balance consideration it has been shown[19] that the molar fraction of monomer 1 in the feed at a given time of reaction, f_1, is relative to the cumulative average mole composition of the copolymer $F_1(\text{cum})$ by:

$$f_1=\frac{f_1^0-XF_1(\text{cum})}{1-X} \qquad (4)$$

where X is the mole degree of conversion defined as:

$$X=1-\frac{M}{M_0}$$

Using equations (3) and (4) values of $F_1(\text{cum})$ for different X values can be generated, and the results compared with the experimental data. Such a comparison is shown in *Figures 3* and *4* for the F–P copolymerization system for two compositions of the initial monomers feed f_F^0 equal to 0.02 and 0.5, respectively.

Figure 3 shows the diagram of the variation of the cumulative F molar fraction in the copolymer with the molar conversion for an initial composition of the monomers feed of $f_F^0=0.02$. As was expected from the kinetic study of the copolymerization at low conversion ($<5\%$)[6], the copolymers prepared at very low conversion are comparatively very rich in F, but according to the classical copolymerization scheme and taking into consideration equations (3) and (4) a dramatic decay of the cumulative copolymer composition, $F_F(\text{cum})$, with increasing degree of conversion is observed. As it can be clearly seen in *Figure 3*, the experimental data obtained by different techniques and media of polymerization fit adequately the diagram predicted by equations (3) and (4) with the simplification considered above. Moreover, the data obtained in the copolymerization carried out in a solution of DMF at 50°C, with a total concentration of monomers of 1 mol l^{-1}, at high vacuum, give the best fit over all the composition intervals. However, the results obtained using the photochemical activation of free radicals from the decomposition of AIBN at 40 and 0°C, are in good agreement if we take into consideration that these data were obtained directly using the samples irradiated in the photocalorimeter, with only a few miligrams of F. In addition, the composition of copolymer

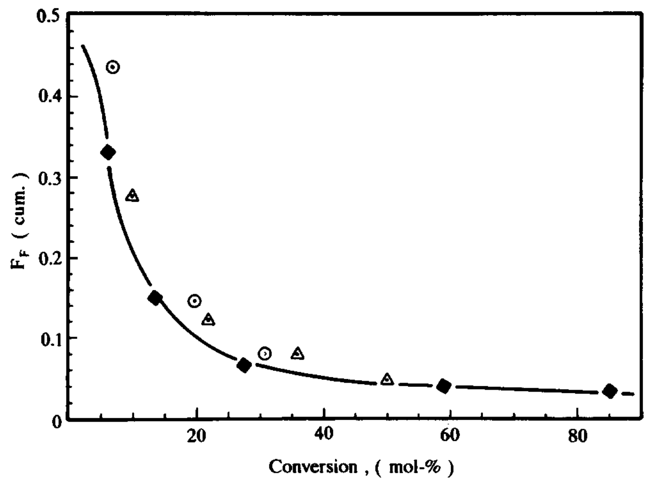


Figure 3 Variation of the cumulative composition of copolymer chains, F_F(cum), as a function of the molar conversion, for the free radical copolymerization of F and P with the monomers feed $f_F^{\circ}=0.02$, under different conditions: (◆) polymerization in DMF solution at 50°C with AIBN as initiator; (⊙) polymerization in bulk with AIBN activated photochemically at 0°C; (△) polymerization in bulk with AIBN activated photochemically at 40°C; (——) diagram predicted by equation (4)

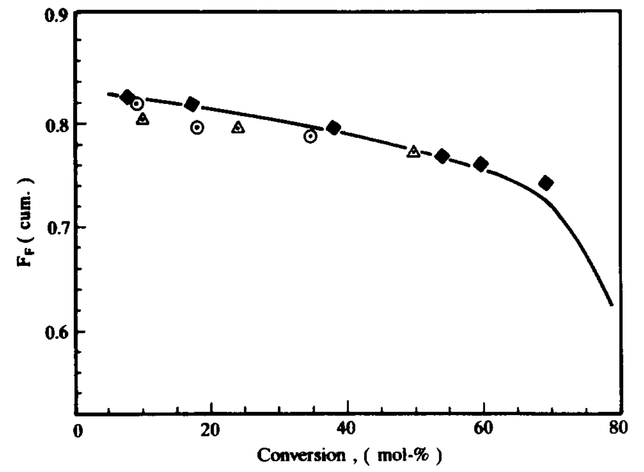


Figure 4 Variation of the cumulative composition of copolymer chains, F_F(cum), as a function of the molar conversion, for the free radical copolymerization of F and P with the monomers feed $f_F^{\circ}=0.50$. The points and line have the same meaning as in *Figure 3*

samples was determined by registering the ^{1}H n.m.r. spectra of the bulk reaction product dissolved in deuterated chloroform without previous isolation and purification of the high molecular weight copolymer species. This was possible because the signals used to evaluate the concentration of F and P units incorporated into a copolymer chain are sufficiently shifted with respect to that of free monomers. These data can also be obtained by the difference between the remaining signals of the acrylic and vinyl protons and those of the side substituents.

It is worth mentioning that due to the much higher value of r_F as compared to r_P, values of f_F of the order of 10^{-9} have to be considered in order to generate the theoretical point for 10% conversion when $f_F^{\circ}=0.02$. This indicates that for $f_F^{\circ}=0.02$ monomer F becomes practically exhausted in the early stages of the reaction, and from then only homopolymerization of P proceeds. The situation is somewhat different when $f_F^{\circ}=0.5$, because f_F remains comparatively high ($=0.125$) even for a conversion as high as 64.7%, but then drops dramatically to 2×10^{-4} at 69.6% and 10^{-10} at 71.3%.

The behaviour of the copolymerization system for an equimolecular mixture of the monomers is completely different from that observed for a composition of $f_F^{\circ}=0.02$. As is shown in *Figure 4*, F_F(cum) remains very high and practically constant [F_F(cum)$\approx$0.78–0.82] over a wide range of conversions and it is necessary to reach degrees of conversion as high as 60 mol% to detect significant variations. The experimental results obtained for all the copolymer samples prepared by homogeneous free radical polymerization in solution or even by photochemical activation of the AIBN, fit fairly well the composition diagram obtained according to equations (3) and (4) which predict a very slow decay of the cumulative molar fraction, F_F(cum), with the degree of conversion up to conversions of ~65%. For conversions higher than this value, a drastic decay of F_F(cum) should be expected, as has been indicated above. We stress here that a deviation of the experimental values of F_F of ~2–3% is within the limits of experimental error provided by the ^{1}H n.m.r. characterization technique[20].

Figure 5 shows the kinetic diagrams from the conversion–time data obtained for the free radical polymerization in a solution of DMF for the two monomer feed compositions studied in the present work. In both cases the conversion increases smoothly with the time of reaction following as a first approach the classical polymerization scheme of free radical polymerization[1,2]. However, a detailed analysis of the diagrams obtained indicated clear differences depending on the concentration of F.

As expected, the degree of conversion reached at a given reaction time is higher for media rich in F as a consequence of the higher reactivity of F in comparison with P. However, the conversion–time data seem to be independent of the initial composition for long polymerization times, after 15–16 h, which correspond to degrees of conversion in the range 65–70%. At longer reaction times both copolymerization systems tend to reach a limiting conversion of ~85%, which was predicted considering the effects of the dead-end polymerization scheme on the decrease of active free radicals for long polymerization times as pointed out above.

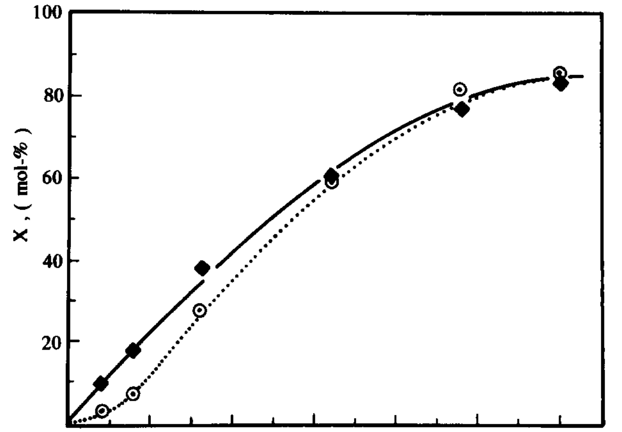


Figure 5 Kinetic diagram of the free radical copolymerization of F and P in DMF solution initiated by AIBN at 50°C: (◆) $f_F^{\circ}=0.50$; (⊙) $f_F^{\circ}=0.02$

Also, the tendency to give the same conversion–time diagram at reaction times of >15 h can be easily explained if we consider that in both cases the concentration of F in the reaction medium is so low that the system becomes practically a homopolymerization process of the remaining P. These data are in good agreement with those of the composition–conversion diagrams shown in *Figures 3* and *4*, since the concentration of F in the feed falls to very low values at conversions around 5 mol% for $f_{\mathrm{F}}^{\circ}=0.02$ and around 65–70% for $f_{\mathrm{F}}^{\circ}=0.50$.

On the other hand, the conversion–time diagram of the copolymerization system with $f_{\mathrm{F}}^{\circ}=0.02$ seems to present an initial induction period in which the average polymerization rate seems to be somewhat lower than at longer reaction times. According to the classical free radical copolymerization scheme, independently of the initiation mode, the propagation step is characterized by the two homopropagation addition reactions, F–F and P–P and the cross-propagation F–P and P–F. It has been widely demonstrated that, in general, the overall rate of copolymerization is lower than those of the homopolymerization of the corresponding monomers[21–23] because the bimolecular cross-termination process is faster than the corresponding homotermination reactions. Considering this fact, in the copolymerization system with $f_{\mathrm{F}}^{\circ}=0.02$, during the first 4 h a conversion degree of only 5 mol% is reached, and according to the statistical distribution of monomeric sequences[6], the main process in this interval is the cross-propagation and probably the cross-termination of F–P units. As has been indicated above, at conversions of >5 mol%, practically all the reaction medium is exclusively P molecules and logically the cross-propagation and cross-termination become negligible, with a corresponding increase in the overall copolymerization rate.

Finally, *Figure 6* shows the variation of the overall copolymerization rate as a function of the degree of conversion. It is clear from this figure that the most noticeable kinetic differences of the copolymerizations with the initial feed compositions analysed appear in the first period of reaction, which corresponds to the consumption of F, mainly through cross-propagation processes in the case of the reaction with $f_{\mathrm{F}}^{\circ}=0.02$, and homo- and cross-propagation for $f_{\mathrm{F}}^{\circ}=0.50$. The most interesting feature is that the instantaneous rate of polymerization for both systems decreases similarly as the conversion increases, and decays smoothly for long reaction times as a consequence of the dead-end polymerization effect.

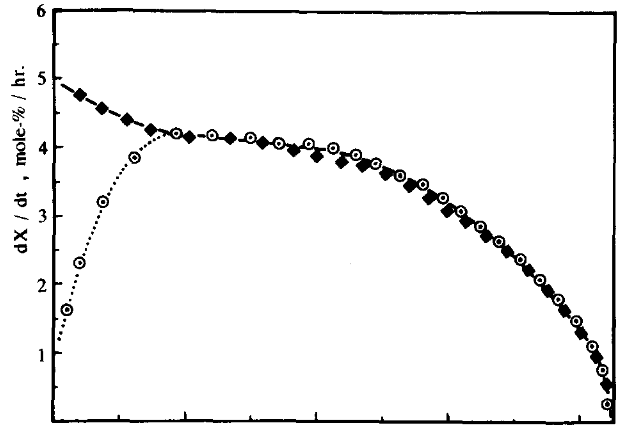


Figure 6 Variation of the instantaneous overall rate of copolymerization, d*X*/d*t*, with the molar conversion for the free radical copolymerization in DMF at 50°C: (◆) $f_{\mathrm{F}}^{\circ}=0.50$; (⊙) $f_{\mathrm{F}}^{\circ}=0.02$

CONCLUSIONS

The experimental data obtained for the copolymerization of F with P under different experimental conditions make clear that the initiation mode (thermal or photochemical decomposition of the free radical source, AIBN) or even the global concentration of reactants (bulk or solution) have little influence on the average composition of copolymer chains, independently of the initial feed composition. However, this is hardly affected by the variation of the feed composition with conversion because of the great difference in the reactivities of F and P radicals and free molecules.

In any case, the variation of the cumulative composition of copolymer chains with the degree of conversion seems to fit the prediction of the integrated copolymerization equation suggested by Skeist, and it is demonstrated that when the $r_i \gg r_j$, such as in the present case, a simplification of Skeist's equation can be applied with minimum error.

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REFERENCES

1 Bevington, J. C. in 'Comprehensive Polymer Science, Vol. 3' (Eds G. C. Eastmond, A. Ledwith, S. Russo and P. Sigwalt), Pergamon Press, Oxford, 1989, p. 65
2 Eastmond, G. C. in 'Comprehensive Chemical Kinetics' (Eds C. H. Bamford and C. F. H. Tipper), Vol. 14, Elsevier, Amsterdam, 1976
3 Mayo, F. R. and Lewis, F. M. *J. Am. Chem. Soc.* 1944, **66**, 1594
4 Hamielec, A. E., MacGregor, J. F. and Pendelis, A. in 'Comprehensive Polymer Science, Vol. 3' (Eds G. C. Eastmond, A. Ledwith, S. Russo and P. Sigwalt), Pergamon Press, Oxford, 1989, p. 17
5 Odian, G. 'Principles of Polymerization', 3rd Edn, Wiley Interscience, New York, 1991
6 Zaldívar, D., Peniche, C., Bulay, A. and San Román, J. *Polymer* 1992, **33**, 4625
7 Burkhart, R. D. and Merrill, J. C. *J. Phys. Chem.* 1969, **73**, 2699
8 Skeist, I. *J. Am. Chem. Soc.* 1946, **68**, 1781
9 Capek, I., Juranicova, V. and Bartoh, J. *Makromol. Chem.* 1983, **189**, 1597
10 O'Driscoll, K. F., Kale, L. T., García-Rubio, L. H. and Reilly, P. M. *J. Polym. Sci., Polym. Chem. Edn* 1984, **22**, 2777
11 Stejskal, J., Kratochvil, P., Strakova, D. and Prochazka, O. *Macromolecules* 1986, **19**, 1575
12 Sastre, R., Conde, M. and Mateo, J. L. *J. Photochem. Photobiol. A* 1988, **44**, 111
13 Sastre, R., Conde, M., Catalina, F. and Mateo, J. L. *Rev. Plast. Mod.* 1989, **393**, 375
14 Mayo, F. R. and Walling, C. *Chem. Rev.* 1950, **46**, 191
15 Billmeyer, F. W. 'Textbook of Polymer Science', Wiley, New York, 1971, p. 330
16 Tobolski, A. V., Rodbers, C. E. and Brickman, J. *J. Am. Chem. Soc.* 1960, **82**, 1277
17 Zaldívar, D., Peniche, C., Gallardo, A. and San Román, J. *Biomaterials* 1993, **14**
18 Meyer, V. E. and Lowry, G. C. *J. Polym. Sci. A* 1965, **3**, 2843

19 Dionisio, J. M. and O'Driscoll, K. F. *J. Polym. Sci., Polym. Lett. Edn* 1979, **17**, 701

20 Bovey, F. A., Jelinski, L. and Mirau, P. A. 'Nuclear Magnetic Resonance Spectroscopy', 2nd Edn, Academic Press, New York, 1988

21 O'Driscoll, K. F. *Makromol. Chem. Macromol. Symp.* 1992, **53**, 52

22 O'Driscoll, K. F. in 'Comprehensive Polymer Science, Vol. 3' (Eds G. C. Eastmond, A. Ledwith, S. Russo and P. Sigwalt), Pergamon Press, Oxford, 1989, p. 161

23 Gallardo, A. and San Román, J. *Polymer* 1993, **24**, 567