Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1991, **1(2)**, 68–70

Mendeleev Communications

'Pseudo Gel-effect' in Radical Copolymerization

Semen I. Kuchanov and Mihail Y. Gelfer*
Department of Polymer Science, Faculty of Chemistry, Moscow State University, Leninskie Gory, Moscow, V-234, USSR

An acceleration in copolymerization reactions which is not associated with the formation of 'networks of entanglements' but is caused by changes in the composition of the monomer feed is described for the first time.

The term gel-effect is used to describe the substantial acceleration of free-radical polymerization at high conversions. It operates during the polymerization of some vinyl monomers in bulk or in concentrated solutions. The well established description of the nature of the gel-effect involves the formation of a 'network of entanglements' of macromolecules, preventing bimolecular termination of macroradicals.[1–3] It is obvious that this phenomenon would disappear owing to dilution in the presence of a sufficient quantity of an inert solvent.[4] However, autoacceleration of the process may be observed at intermediate or high conversions in the free-radical copolymerization of vinyl monomers under dilute conditions. We now present arguments in support of this phenomenon and provide experimental evidence.

It is possible that during the copolymerization, along with the overall decrease in rate, caused by consumption of the monomer, a rate increase resulting from a change in monomer feed composition may occur. In fact an initial copolymerization rate depending on the composition of the reaction mixture has been established experimentally for a number of systems.[1–5] Thus the increase as the conversion proceeds of the proportion of the monomer whose content promotes the copolymerization rate increase may cause the acceleration process. Conditions for such a change in the composition of the monomer feed may be predicted by the well established copolymerization theory; they depend on the initial monomer feed composition and on the kinetic parameters of the process.

If the system follows traditional kinetics the overall rate of copolymerization will depend in a first-order manner on the monomer concentration. The coefficient of proportionality depends on the monomer feed composition; if this does not change with conversion the inherent rate $W_p/[M]$ {W_p = rate of monomer consumption (polymerisation rate); [M] = monomer concentration} will remain constant during the entire process. If the inherent rate increase caused by a change in monomer feed composition is large enough the overall rate of the process will increase. The acceleration of the copolymerization arising for these reasons may be called the 'pseudo-gel effect'.

It should be mentioned that for some systems there may exist a so-called 'azeotrope'; the monomer feed composition coincides with the polymer composition. Under 'azeotropic' conditions the composition of the reaction mixture remains constant during the entire process.[5] It is clear that under such conditions a 'pseudo-gel effect' would not arise. Experimental support for the non-occurrence of a 'pseudo-gel effect' under these conditions would support our suppositions.

To study the 'pseudo-gel effect' experimentally we have chosen the copolymerization of styrene (St) with butyl acrylate (BA) in benzene solution.

According to literature data, the St–BA system should provide suitable conditions for the appearance of the 'pseudo-gel effect',[6–8] benzene having been shown to be an inert solvent for this system.[6]

A technique developed by us has been used in this paper. This technique enables isothermal calorimetry to be used for investigating the copolymerization over a wide range of conversions.[9] Our experimental data prove that the dilution used (benzene, 80% molar proportion) is sufficient to avoid the traditional 'gel-effect'. In fact, the acceleration occurs neither in the homopolymerization of the monomers separately nor in the copolymerization under 'azeotropic conditions' (Figs. 1, 2). In contrast, for the systems with molar ratios of BA to St of 9:1 and 19:1, a large acceleration takes place. For the system with a molar ratio of BA to St of 19:1 the inherent rate increases more than three-fold, and the overall rate is almost doubled (Figs. 1, 2). In this case, the cause of the autoacceleration is the 'pseudo-gel effect'.

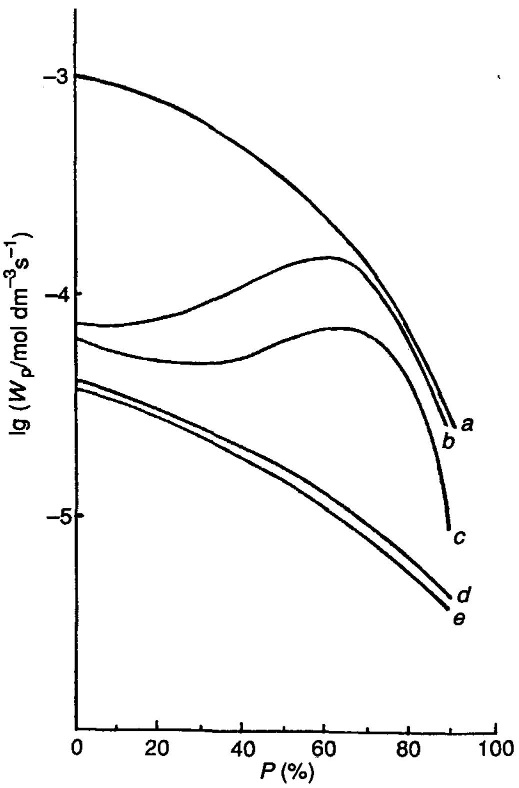

Fig. 1 Kinetic curves for the copolymerization of butyl acetate (BA) and styrene (St) at 60 °C in the presence of azoisobutyronitrile (AIBN) (5 g dm^{-3}). Molar proportion of BA in monomer feed composition: curve *a*, 1·0; *b*, 0·95; *c*, 0·90; *d*, 0·23 (azeotrope); *e*, 0.0.

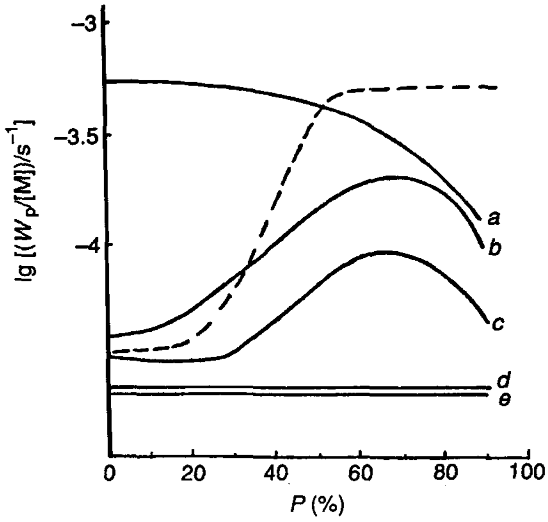

Fig. 2 Inherent rate of copolymerization of butyl acrylate and styrene *vs.* conversion (*P*); conditions and labelling of curves as for Fig. 1. Dashed line: inherent rate of copolymerization from the data in ref. 8 *vs.* conversion.

In the homopolymerization of BA in benzene the inherent rate of polymerization, $W_p/[M]$, decreases with conversion. We have shown by an additional experiment that this effect remains in the presence of the chain-transfer agent CBr_4. A decrease in the inherent rate of copolymerization at high conversions also occurs in the copolymerizations in systems with a large BA content.

This effect may be connected with a phenomenon which has already been described in the literature.[10,11] The formal kinetic order for the monomer determined from the dependence of the initial rate of BA homopolymerization in benzene on the BA concentration is considerably greater than unity and equals 1.7.

Taking the law of mass action into account, assuming a first-order dependence on monomer concentration during the reaction overall, and supposing that the dependence of the copolymerization rate on the monomer feed composition is the same for both high and low conversions one can calculate the rate change with conversion. Knowing the initial rate of copolymerization for a number of monomer feed compositions and calculating the monomer feed composition it is possible to estimate the copolymerization rate for the present conversion. The differential kinetic curve for an initial BA to St ratio of 9:1 calculated from the data in ref. 8 is presented in Fig. 2. The experimentally determined acceleration is considerably lower than the calculated one.

Therefore, the 'pseudo-gel effect' is masked by a side phenomenon, decreasing its maximum value. Even in this case it is not negligible, however.

During bulk copolymerization or copolymerization in concentrated solutions the 'pseudo-gel effect' and the traditional 'gel-effect' may occur simultaneously. This should be taken into account in studies of copolymerization at high conversions.

We thank Academician V. A. Kabanov, Professor Y. D. Semchikov and Assistant Lecturer B. A. Korolev for interesting discussions.

Received in USSR, 21st January 1991
Received in UK, 14th March 1991; Com. 1/00347J

References

1 P. S. Flory, *Principles of Polymer Chemistry*, Cornell University Press, New York, 1953, p. 124.

Mendeleev Commun., 1991, 1(2), 68–70

2 E. Tromsdorf, H. Kohle and P. Lagelly, *Makromol. Chem.*, 1947, **1**, 169.
3 K. Ito, *J. Polym. Sci., Polym. Chem. Ed.*, 1975, **13**, 401.
4 G. Schulz and G. Harboth, *Macromol. Chem.*, 1947, **1**, 106.
5 C. H. Bamford, W. G. Barb, A. D. Jenkins and P. F. Onyon, *The Kinetics of Vinyl Polymerization by Radical Mechanisms*, Academic Press, New York, 1958, p. 156.
6 F. Tudos, C. K. Kaszar and T. Foldes-Bereznich, *Eur. Polym. J.*, 1984, **20**, 395.
7 S. B. Bradbury and A. W. Melville, *Proc. Roy. Soc. London, Ser. A*, 1954, **22**, 456.
8 F. Tudos, *J. Macromol. Sci. Chem. A*, 1985, **22**, 1571.
9 S. I. Kuchanov, M. Y. Helfer and B. A. Korolev, All-Union Conference Rapid Polymerization, Gor'kii, Thesis, 1989, p. 9.
10 G. Kaszas, T. Foldes-Bereznich and F. Tudos, *Eur. Polym. J.*, 1983, **19**, 469.
11 J. Pavlinec, M. Jekgusova and S. Flovian, *Eur. Polym. J.*, 1982, **18**, 279.