

Gelation in the Radical Polymerization of Dimethyl Diallyl Ammonium Chloride

G. V. Kozlov,¹ Y. A. Malkanduev,¹ G. E. Zaikov²

¹Kabardino-Balkarian State University, Chernyshevsky St. 173, Nalchik 360004, Russia

²Institute of Biochemical Physics, Russian Academy of Sciences, Kosygin St. 4, Moscow 119991, Russia

Received 13 May 2003; accepted 22 January 2004

DOI 10.1002/app.20502

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Within the framework of an irreversible aggregation model on a sample of polydimethyl diallyl ammonium chloride, we demonstrated that gelation occurred on a transient part from the autoacceleration stage until the copolymerization stage. During part of the autoacceleration, the polymer solution was in a sol state on the segment of

autoacceleration. Therefore, the use of the term *gel effect* in reference to the beginning of the reaction did not seem quite justified. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1394–1396, 2004

Key words: radical polymerization; gelation

INTRODUCTION

A large amount of attention has been given to the study of gelation during polymer synthesis. However, in radical polymerization, there are several points of view on the definition and position of this effect on the curve of conversion degree (Q) versus time (t). By definition, the *gel point* is the point at which the solution begins to have some properties of a solid (e.g., elasticity, brittleness).¹ During radical polymerization, there is a gel-effect point, or transition from, the initial part of polymerization to the autoacceleration part.² In the physics of polymers, there is a more exact definition of *gel point* as the point at which the cluster subtending a system (spreading from one edge of the system to the other) is formed.^{3,4} The different approaches to and definitions of this effect can cause uncertainty in its explanation. Therefore, the purpose of this study was to determine the gelation point position on a Q - t curve in terms of the definition found in refs. 3 and 4 and with the help of an irreversible aggregation model for the radical polymerization of a sample of dimethyl diallyl ammonium chloride (DMDAACH).⁵

EXPERIMENTAL

Poly(dimethyl diallyl ammonium chloride) (PDM-DAACH) was synthesized in aqueous solution at initial concentrations of the monomer (C_0) of 4.5, 5.0, and 5.5 mol/L (0.727–0.888 wt %). Initiation was made by

the thermal decomposition of ammonium persulphate with an initiator concentration of 5×10^{-3} mol/L. Q was determined by a calorimetric method. The polymerization was carried out at 333 K.

The molecular weight (MW) of PDMDAACH was determined according to the Mark–Houwink–Sakurada equation:⁶

$$[\eta] = 1.12 \times 10^{-4} \times \text{MW}^{0.82 + 0.07} \quad (1)$$

where $[\eta]$ is the intrinsic viscosity.

The value of the fractal dimension (D) of the macromolecular coil in solution was determined from the following equation:⁷

$$D = \frac{3}{1 + a} \quad (2)$$

where a is the exponent from the Mark–Houwink–Sakurada equation, equal to 0.82 for PDMDAACH [eq. (1)].

RESULTS AND DISCUSSION

The gelation effect, treated as the formation of a cluster subtending a system, resulted in essential changes in the parameters describing this system for the gelation point.³ So, a motion rate (γ) of the clusters (macromolecular coils) with mass (m) is assumed equal to (3):

$$\gamma = m^\alpha \quad (3)$$

For the gelation point, the exponent α changes the sign from negative to positive. This means that up to

Correspondence to: G. E. Zaikov (chembio@sky.chph.ras.ru).

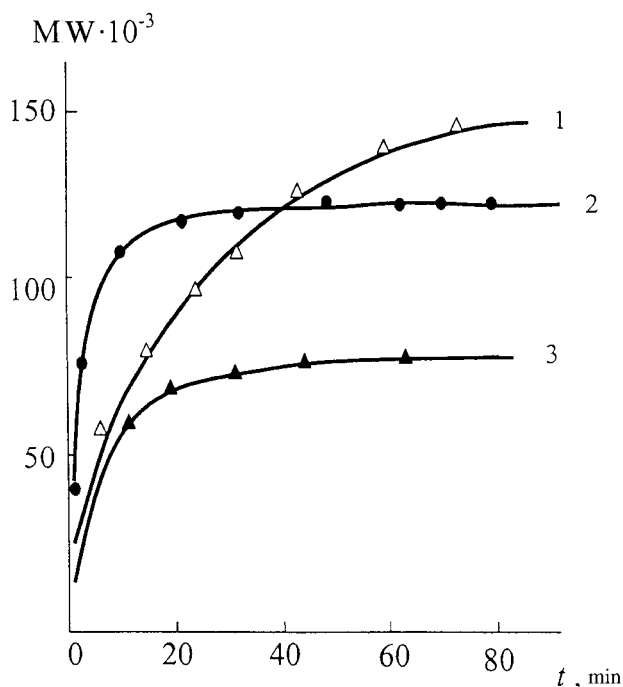


Figure 1 Dependences of MW on the reaction time for the polymerization of DMDAACH at C_0 values of (1) 4.5, (2) 5.0, and (3) 5.5 mol/L.

the gelation point, the smaller clusters have a greater mobility; beyond the gelation point, the subtending cluster have the greatest mobility because its weight is greater than the weights of the macromolecular coils.^{3,4}

A similar sharp change in the exponent ω in the Smoluchovski scaling relationship for the gelation point occurs within the framework of the kinetic gelation concept.³ At $\omega < 0.5$, for all distributions of the cluster size, the common scaling and average cluster size grow regularly with time; beyond the gelation point ($\omega > 0.5$), this scaling is broken, and the greatest cluster grows quickly.³

Finally, for the gelation point, the static general characteristic of the system are changed. Theoretically³ and experimentally,⁸ it has been shown that the value of D changes from about 1.5 to 2.1 for a typical macromolecular coil in solution,⁹ up to about 2.5, which describes a Witten-Sander cluster.³

As calculated according to eq. (2), the value of D for PDMDAACH was about 1.65. Such a value of D uniquely defined the formation mechanism of macromolecular coil PDMDAACH in solution as a diffusion-limited aggregation to a cluster-cluster mechanism.¹⁰ Within the framework of this model, the dependence of the coil gyration radius (R_g) from a reaction duration of time t was determined as follows:¹¹

$$R_g \approx t^{1/Z} \quad (4)$$

where Z is the exponent connected with D and α by the following relationship:¹¹

$$Z = D(1 - \alpha) - (d - 2) \quad (5)$$

where d is the dimension of Euclidean space in which one fractal is considered. Apparently, in our case, d was equal to 3.

Within the framework of the fractal analysis, it was possible to obtain (for the same polymer):¹⁰

$$R_g \approx N^{1/D} \approx MW^{1/D} \quad (6)$$

where N is the polymerization degree.

Finally, the exponents α and ω were connected to each other by the following equation:³

$$2\omega = \alpha + \frac{d - 2}{D} \quad (7)$$

Thus, with the dependences of $MW(t)$ and plotting according to the data from ref. 12 and shown in Figure 1 and eqs. (4)–(7), we were able to determine the values of the exponents Z , α , and ω . On the basis of the boundary values reviewed previously, we were able to determine whether or not gelation occurred on a given part of the Q – t kinetic curve. However, first, we discuss the classification of these parts, which are schematically shown in Figure 2. The Q – t curves for PDMDAACH had a sigmoidal shape typical for radical polymerization processes.^{5,12} In Figure 2, point A cor-

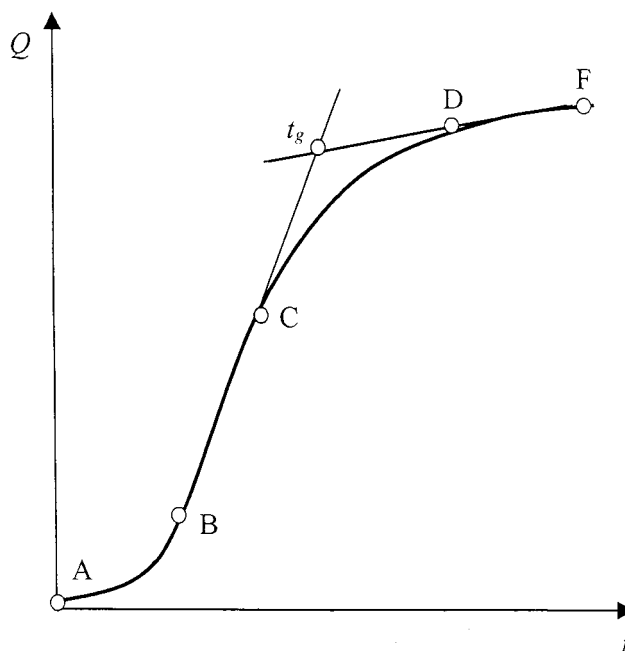


Figure 2 Scheme of part placement on the Q – t curve and the definition of t_g for the radical polymerization of DMDAACH.

TABLE I
Values of the Exponents of an Irreversible Aggregation Process on Parts B–C and C–D of the Q - t curve and the Relative Mobility of Clusters on Part B–C for PDMDAACH

C_0 (mol/L)	Part B–C				Part C–D		
	z	α	ω	γ	Z	α	ω
4.5	3.10	-1.48	-0.435	33.1	-0.392	0.757	0.682
5.0	5.95	-3.60	-1.497	0.25	-0.458	0.783	0.695
5.5	8.63	-4.84	-2.120	0.015	-0.598	0.839	0.723

responds to the beginning of polymerization ($t = 0$), and point B corresponds to the initial termination and transition to acceleration. Part C–D characterizes the transition from autoacceleration to copolymerization at part D–F (we retained the conventional notation of the parts). We graphically obtained the gelation point and the time corresponding to it (t_g) as the point of tangential intersection from parts B–C and D–F (Fig. 2).

In Table I, we list the values of the exponents Z , α , and ω for parts B–C and C–D. As follows from the data in Table I, for part B–C (autoacceleration), $\alpha < 0$ and $\omega < 0.5$. This means that in all parts of the autoaccelerations, gel formation did not occur, and the solution was in a sol state. The opposite was observed for the exponents α and ω for part C–D. In this case, $\alpha > 0$ and $\omega > 0.5$, which means gel formation occurred. For part C–D, the value of MW reached asymptotic values; that is, a point was reached where MW was constant. Therefore, for the time corresponding to point C, $R_g \approx MW^{1/1.65}$, and for the time corresponding to point D, $R_g \approx MW^{1/2.45}$. In other words, this was the transition from $D = 1.65$ (cluster–cluster mechanism) to $D = 2.5$ (particle–cluster mechanism). Therefore, as shown in Figure 2, the graphic definition of t_g was quite justified.

In Table I, the values of the cluster rate (δ) in solution (relative units) as calculated according to eq. (3) are listed. As shown in Table I, the increase in C_0 resulted in a very sharp reduction in γ ; the change in C_0 from 4.5 up to 5.5 mol/L decreased γ by 2300 times. Also, it follows from the data in Table I that the increase in C_0 did not mean that the polymerized solution was approaching the gelation point; as C_0 increased, ω decreased.

CONCLUSIONS

Thus, within the framework of an irreversible aggregation model on a sample of PDMDAACH, we demonstrated that gelation occurred in a transient manner from autoacceleration up to the stage of copolymerization. In autoacceleration, the polymer was in a sol state. Therefore, the use of the term *gel effect* with reference to the beginning of the autoacceleration stage did not seem quite justified.

References

1. The Encyclopedia of Polymers; Kargin, V., Ed.; Soviet Entsiklopedia: Moscow, 1972; Vol. 1, p 1223.
2. Bityurin, N. M.; Genkin, V. N.; Zubov, V. P.; Lachinov, M. B. *Vysokomol Soedin A* 1981, 23, 1702.
3. Botet, R.; Jullien, R.; Kolb, M. *Phys Rev A* 1984, 30, 2150.
4. Kolb, M.; Herman, H. J. *J Phys A* 1985, 18, L435.
5. Topchiev, D. A.; Malkanduev, Y. A. *Cationic Polyelectrolytes of Set N,N-Dialkyl-N,N-Diallylammonium of Halogens: Features of Formation Processes, Properties, and Application*; KBGU: Nalchik, Russia, 1997; p 182.
6. Timofejeva, G. J.; Pavlova, S. A.; Wandrey, C.; Jaeger, W.; Hahn, M.; Linow, K.-J.; Gornitz, E. *Acta Polym* 1990, 41, 479.
7. Karmanov, A. P.; Monakov, Y. B. *Vysokomol Soedin B* 1995, 37, 328.
8. Kobayashi, M.; Yoshioka, T.; Imai, M.; Itoh, Y. *Macromolecules* 1995, 28, 7376.
9. Baranov, V. G.; Frenkel, S. Y. Brestkin, Y. V. *Dokl Akad Nauk* 1986, 290, 369.
10. Kokrevich, A. G.; Gravitis, Y. A.; Ozol-Kalnins, V. G. *Khimija Drevesiny* 1989, No. 1, 3.
11. Kolb, M. *Phys Rev Lett* 1984, 53, 1653.
12. Yanovskij, Y. G.; Topchiev, D. A.; Barancheeva, V. V.; Malkanduev, Y. A.; Kabanov, V. A. *Vysokomol Soedin A* 1988, 30, 1226.