

Here, S_F is the free-volume contribution and S_R the remaining contributions to the concentration dependence. These two terms and their sum are shown in Table I and confirm the smooth variation of concentration dependence and the lack of unique power-law dependences over significant ranges of concentration. Over the range of values of N and ϕ studied in this work, the power-law dependence goes from -0.18 to -1.1 . At the highest concentrations, where the power-law dependence is greatest, it will be seen that the major contribution comes from the free-volume term S_F . The non-free-volume term S_R is proportional to ϕ and clearly cannot remain even approximately constant over significant ranges of ϕ . We further note that the non-free-volume term S_R is not independent of N as would be required by the suggestion of NLNKWY.

In summary, the simulation results, like the experimental results of WNKY and MAF, exhibit a wide range of power-law dependence of D upon concentration and a complete absence of regions of constant power-law dependence. Further, the concentration dependence of D appears to be dominated by local free volume, as is also suggested by the experimental results of MAF. However, the non-free-volume term fails to exhibit the region of constant (-1.75) power-law dependence observed in the analysis of MAF and is not independent of molecular weight as suggested by NLNKWY.

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References and Notes

- (1) Doi, M.; Edwards, S. F. *J. Chem., Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
- (2) de Gennes, P.-G. *Macromolecules* **1976**, *9*, 587, 594; *J. Chem. Phys.* **1971**, *55*, 572.
- (3) Wesson, J. A.; Noh, I.; Kitano, T.; Yu, H. *Macromolecules* **1984**, *17*, 782.
- (4) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.
- (5) van Meerwall, E. D.; Amis, E. J.; Ferry, J. D. *Macromolecules* **1985**, *18*, 260.
- (6) Kranbuehl, D. E.; Verdier, P. H. *Macromolecules* **1984**, *17*, 749.
- (7) Nemoto, N.; Landry, M. R.; Noh, I.; Kitano, T.; Wesson, J. A.; Yu, H. *Macromolecules* **1985**, *18*, 308.
- (8) Hilhorst, H. J.; Deutch, J. M. *J. Chem. Phys.* **1975**, *63*, 5153.
- (9) Kranbuehl, D. E.; Verdier, P. H. *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1980**, *21*, 195.
- (10) We are grateful to one of the referees for suggesting that this explanation of the choice of move processes be made.

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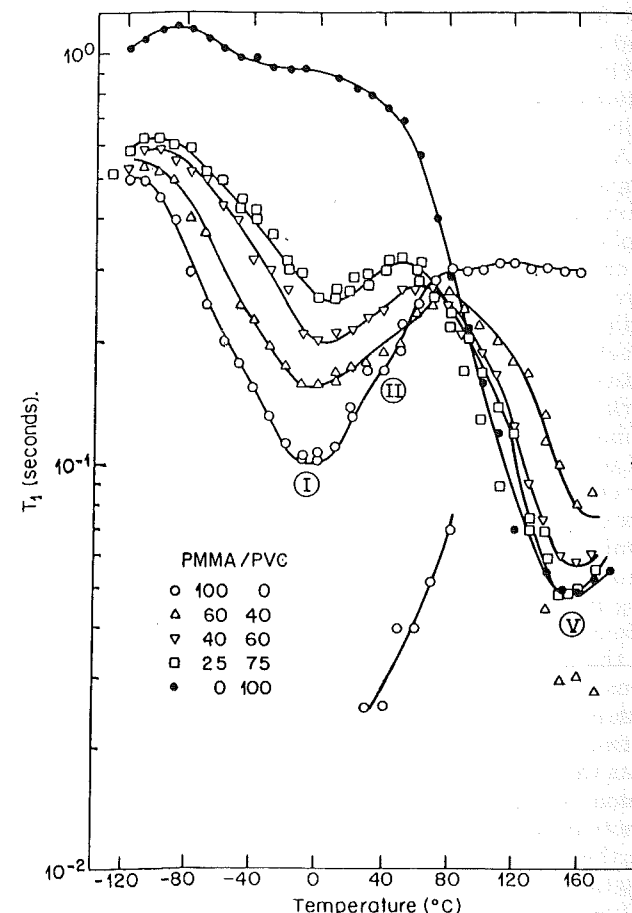
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CORRECTIONS

Brigitte Albert, Robert Jérôme, Philippe Teyssié, Gerard Smyth, Noel G. Boyle, and Vincent J. McBrierty*: Investigation of Compatibility in Syndiotactic Poly(methyl methacrylate)/Poly(vinyl chloride) Blends. Volume 18, Number 3, March 1985, p 388.

Figure 1 of this paper incorrectly portrays the T_1 data for the 60/40 s-PMMA/PVC blend. The correct figure is presented herein.



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"Spontaneous" Vinyl Polymerization of 2-Vinyl-2-oxazolines

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ABSTRACT: 2-Vinyl- and 4,4-dimethyl-2-vinyl-2-oxazolines were polymerized via the opening of the olefinic bond when they were alkylated with alkyloxonium salts or superacid esters. The polymers produced had a general structure of poly[1-(3-alkyl-2-oxazolinium-2-yl)ethylene]. Concerning the mechanism of this peculiar polymerization, it has been assumed that a 3-alkyl-2-vinyl-2-oxazolinium salt, which is produced by alkylation initiation, is so reactive that it enters into an anionic polymerization initiated by the nucleophilic attack of free monomer. The reaction of the oxazolinium ring of the product polymer with amine was also examined.

Introduction

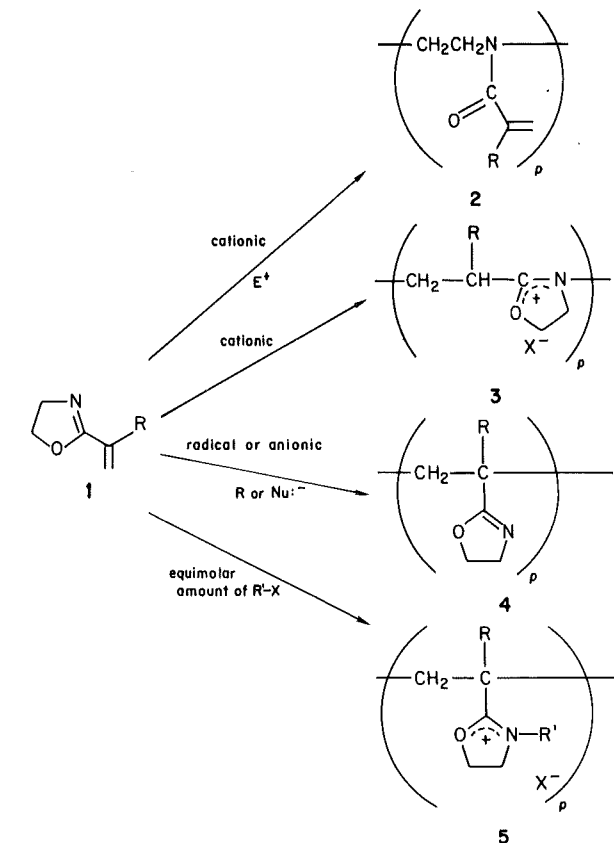
Reactivities of various 2-substituted 2-oxazolines in cationic ring-opening polymerization have been studied quite extensively.¹ Among them, 2-vinyl- ($R = H$ in 1) and 2-isopropenyl-2-oxazolines ($R = Me$ in 1) are polymerized by three reaction modes: cationic ring-opening polymerization to poly[(*N*-acryloyl(or methacryloyl)imino)ethylenes] 2,²⁻⁴ cationic polymerization to give ring-preserved polymers 3,⁵ and olefinic polymerization via a radical^{2,4,6} or anionic⁵ mechanism to produce poly[(2-oxazolin-2-yl)alkenes] 4 (Scheme I).

In this paper we describe a fourth mode of polymerization of 2-vinyl-2-oxazolines which occurs by the *N*-alkylation of the 2-oxazoline moiety with strong alkylating agents such as trialkyloxonium salts, alkyl sulfates, and alkyl sulfonates. The product polymers have a general structure of poly[1-(3-alkyl-2-oxazolinium-2-yl)ethylene] 5, which cannot be produced in pure form by direct alkylation of the vinyl polymer of 4. The new mode of polymerization is related to the "spontaneous" polymerization of 2- and 4-vinylpyridines.⁷⁻¹¹

Results and Discussion

"Spontaneous" Polymerization. It is known that an equimolar reaction of 2-substituted-2-oxazoline with alkylating agents or strong Brønsted acids produces stable 3-alkyl-2-oxazolinium salts or 3-protio-2-oxazolinium salts in high yields.^{4,12} The salts correspond to the propagating species of the cationic ring-opening polymerization of 2-oxazolines, and in fact they induce the cationic ring-opening polymerization of 2-oxazolines. In the present study, the alkylation of 2-vinyl- (1a) and 4,4-dimethyl-2-vinyl-2-oxazolines (1b) was tried by using four kinds of strong alkylating agents 6, i.e., so-called Meerwein reagents

Scheme I



6a-1 and 6a-2 and superacid esters 6b-1 and 6b-2. As soon as 1 was added to a solution of 6 in CH_2Cl_2 at $0^\circ C$, a white