Diffusion Effects in Initiator Decomposition in Highly Viscous and Macromolecular Solutions

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Diffusional limitations in single bond and multibond initiators were experimentally investigated. The concept of "microviscosity" was proposed to account for diffusional resistance in different media. This was then used to obtain a unified correlation of the diffusional phenomena regardless of the nature of viscogen. Parameters related to the kinetic and diffusive processes were evaluated and interpreted giving clear fundamental and pragmatic implications of the findings.

SCOPE

Initiation in free radical polymerization starts by decomposition of initiator. In most cases, such decomposition reactions occur in high viscosity media; for example, in graft polymerizations, polymer modification reactions carried out in solutions, etc.

Two kinds of initiators can be conceived. In an initiator such as AIBN, the decomposition results in simultaneous scission of two C—N bonds and is accompanied by the elimination of a nitrogen molecule. Therefore, subsequent recombination of fragments does not give back the original molecule. However, in a one bond initiator such as NAT, decomposition occurs by scission of one bond in each step. Recombination within the primary cage can thus yield the original molecule. The diffusional influences significantly affect the decomposition process of a single bond initiator since the process of recombination and the diffusive separation compete with each other.

There is no prior study which provides a framework for analysis of diffusional limitations in initiator decomposition reactions arising in pragmatically important high viscosity systems, especially in polymer solutions. The present paper bridges this important gap by providing extensive experimental data on decomposition of typical single bond and multibond initiators in a variety of media. It also provides a theoretical framework within which such processes could be analyzed.

CONCLUSIONS AND SIGNIFICANCE

An experimental investigation of the decomposition of a typical two bond initiator [AIBN] and a one bond initiator [NAT] was undertaken in three media; viz., polyethylene glycols, polyacrylonitrile solutions in DMF and glycerol solutions in DMF. A kinetic model was proposed for the analysis of the decomposition, recombination and diffusive separation processes. The rate constant for diffusional separation of initiator fragments was proposed to be calculated by Smoluchowski relation.

In order to account for the diffusional resistance in different environments created by different types of viscogens, a unifying concept of microviscosity (η^*) was proposed. A method to calculate (η^*) from easily available physico-chemical data was proposed.

The governing kinetic parameters for decomposition reaction and recombination reaction as well as for diffusive separation were evaluated. It was found that for a multibond initiator such as AIBN, the rate constant is independent of the viscosity of the medium. In the case of one bond initiator such as NAT, a number of interesting conclusions emerged. The results in polyethylene glycol media show that increasing chain length above a threshold value has no influence on the diffusion of fragments from the cage, indicating that segmental motion controlled the diffusional process. Comparison of kinetic data for glycerol and polymer solutions in DMF indicated that in the former case the reduction in rate constant was very significant. Use of (η^*) evaluated by the method proposed in this paper provided unique plots which were helpful in correlating the diffusional effects in decomposition processes irrespective of the nature of viscogen used.

The conclusions arrived at are of interest from a fundamental view point since they reveal interesting observations concerning the manner in which diffusional phenomena take place in environments created by different viscogens. These are also of considerable pragmatic interest since in the modelling of polymerization reactors, a simple approach to account for the initiator decomposition process in a continuously changing environment emerges.

INTRODUCTION

Initiation in free radical polymerization involves decomposition of initiator and subsequent reaction between the initiator fragments and the monomer. Of the two, the former has been established to be the rate controlling step. The literature on decomposition kinetics of initiators is abundant and well documented (Masson, 1975). However, except for a few publications (Kulkarni et al., 1979; De Schrijver, 1966; Messerle, 1966), no systematic efforts have been made to study the role of viscosity in the initiator decomposition process. It is therefore not surprising that to date there exists no theory which can predict the decomposition constant of an initiator as a function of the

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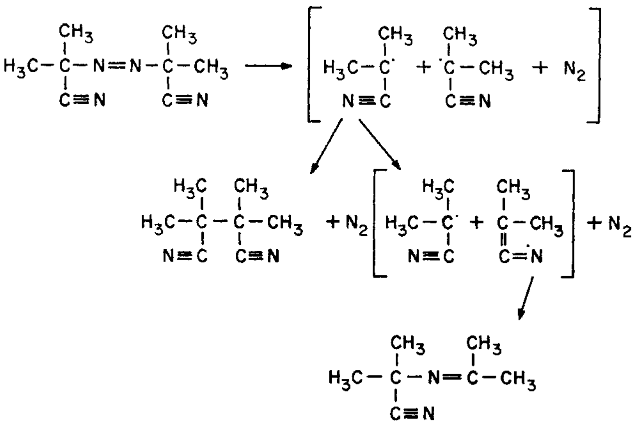
viscosity of the medium. A study of this kind would be of great relevance in understanding the kinetics of graft copolymerization and other polymer modification reactions in which initiation occurs in a high viscosity medium; for example, in the case of grafting of methylmethacrylate on polyisoprene carried out by dissolving the polymer in the monomer and initiated by benzoyl peroxide (Allen, 1956).

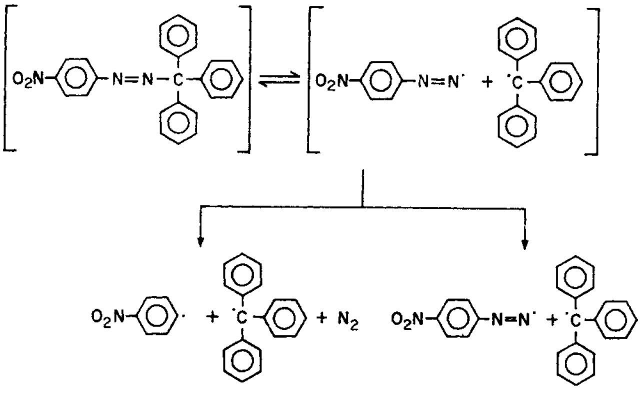
In an earlier paper (Kulkarni et al., 1979), the effect of the nature of the solvent and of the viscosity of the medium on the kinetics of decomposition of azobisisobutyronitrile (AIBN) was discussed. The existence of an isokinetic temperature was unequivocally established and it was shown that the decomposition constant is unaffected by the viscosity of the medium. AIBN is a two bond initiator. Its decomposition occurs by simultaneous scission of two C—N bonds and by the elimination of a nitrogen molecule.



(1)

It is clear from the above reaction sequence that none of the cage return reactions lead to the formation of the parent molecule.

On the contrary, the decomposition of one bond initiator such as p-nitrophenylazotriphenyl methane (NAT), occurs by scission of one bond in each step. The reaction sequence is indicated below.



(2)

The effect of the viscosity of the medium on the decomposition kinetics of one bond initiator such as NAT is not easy to predict and has not been widely studied.

This is probably due to the fact that the decomposition kinetics of NAT is affected by the nature of the medium as well as the viscosity of the medium and it is not possible to estimate how each of the parameters influences the decomposition kinetics. Pryor and Smith (1970) studied the decomposition kinetics in a series of long chain hydrocarbons. The chemical nature of the medium, thus remained unchanged. The results of the study indicate that the decomposition constant decreased very rapidly with increasing number of carbon atoms in the range C_5 to C_{10}, whereas the subsequent decrease in the decomposition constant was much less as the number of carbon atoms increased from C_{12} to C_{18}. This indicates that the efficiency of the cage return process reaches a plateau after a critical chain length is reached. It is therefore expected that if the chain length be sufficiently increased, any further increase in the chain length should have no effect on the decomposition constant irrespective of an increase in viscosity. In order to test this hypothesis we studied the decomposition kinetics of NAT in a series of high molecular weight polyethylene glycols.

It is reasonable to assume that decomposition kinetics of any initiator will depend upon the type of initiator, relative rates of diffusion of fragments out of the cage and recombination within the cage. A detailed account of the importance of cage effects in free radical polymerization reactions can be found in the classical monograph by Bevington (1961). Diffusion-controlled reactions are also discussed widely in literature (Noyes, 1961; North, 1974; Allen and Patrick, 1974). These treatments indicate qualitatively the likely role of viscosity of the medium. However, even to date no quantitative treatment exists which would correlate the rate of decomposition with the viscosity of the medium, irrespective of the nature of the characteristics of the additive which causes an increase in viscosity, i.e., the viscogen. It is the purpose of this communication to bridge this gap.

THEORETICAL CONSIDERATIONS

Development of a Model

Following mechanism is proposed for the decomposition of the initiator (Pryor and Smith, 1970):

$$\begin{array}{lll} \text{Initiator} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} & [\text{Cage I}] & \overset{k_d}{\rightarrow} \text{free radicals} \\ & \downarrow k_\beta & \\ & [\text{Cage II}] + \text{small molecules} & \end{array} \qquad (3)$$

Here, k_1 and k_{-1} denote respectively the rate constants for the forward and backward reaction leading to products in cage I. k_d and k_β denote the rate constants for the formation of free radicals and products of cage II, respectively.

If we assume that the rate of reaction follows a linear kinetics, the overall or the observed rate constant can be deduced as:

$$k = \frac{k_1(k_d + k_\beta)}{k_{-1} + k_d + k_\beta} \qquad (4)$$

Note that Eq. 4 represents the decomposition kinetics of a multibond initiator (such as AIBN) and a single bond initiator (such as NAT). In the case of AIBN, there is no recombination in cage I to yield the parent molecule and here $k_{-1} = 0$. The equation can be reorganized in the following form:

$$\frac{1}{k} = \frac{k_{-1}}{k_1 \cdot k_d}\left[\frac{1}{1 + k_\beta/k_d}\right] + \frac{1}{k_1} \qquad (5)$$

The role of viscosity on the decomposition constant of an azo initiator depends on the relative magnitudes of k_β and k_d. In the case of AIBN (Eq. 1), escape of nitrogen molecule from cage I is instantaneous. Thus, in such a case where $k_\beta >> k_d$, the observed rate constant will be independent of the viscosity of the medium. This is true for any multibond initiator. For a single bond initiator such as NAT (Eq. 2), the β scission process becomes the rate-controlling step. Thus, if k_d be the only rate constant affected by the viscosity of the medium and $k_\beta << k_d$, then:

$$\frac{1}{k} = \frac{1}{k_1} + \frac{k_{-1}}{k_1}\frac{1}{k_d} \qquad (6)$$

In Eq. 6 k_d is the rate constant for diffusion of initiator fragments out of the cage. The most widely known treatment of diffusion-controlled reactions was originally developed by Smoluchowski (Allen and Patrick, 1974) to account for the rates of coagulation of colloid particles. In this case, a reactant particle is regarded as a spherical sink, that is a center to which all other particles move along a concentration gradient. This poses a conceptual difficulty in that the other particles will not themselves be sinks in the same sense. The details of the model for absolutely diffusion-controlled reactions can be found in the monograph by Allen and Patrick (1974). The rate constant k_d can be obtained as:

$$k_d = \frac{N}{1000} \; 4\,\pi\, D\, R_1 \qquad (7)$$

where N is the Avogadro number, D is the diffusivity and R_1 is the radius of the reacting molecule. Equation 7 can be of course refined. However, it can be shown that such refinements do not result in very significant changes in the net prediction. In order to deduce the intrinsic kinetic rate constant $1/k_1$, we may write Eq. 6 as:

$$\frac{1}{k} = \frac{1}{k_1} + \frac{1}{\alpha\, D} \qquad (8)$$

where

$$\alpha = \frac{k_{-1}}{k_1}\,\frac{N}{1000} \; 4\,\pi\, R_1 \qquad (9)$$

α will be a constant for a given system. It is possible to change D by changing the diffusional resistance in the given medium. Usually, at a given temperature, viscosity of the medium determines the diffusional resistance. In the present case, we shall show that this viscosity term needs to be carefully defined and estimated depending on the system characteristics. We shall now propose methods for such estimations.

Development of Concept of "Microviscosity"

Diffusion of low molecular weight species in liquids can be classified into three categories according to the phenomenological behavior. The characteristics of each differ significantly and failure to recognize this can lead to erroneous data interpretation.

Diffusion in Ordinary Low-Viscosity Systems

Consider first the case of diffusion of NAT fragments in dimethylformamide. This is the case of diffusion of a low molecular weight species in a low molecular weight-low viscosity medium. Diffusive transport in such systems is adequately described by the Stokes-Einstein equation; i.e., $D\eta/T$ can be assumed to be constant.

Diffusion in Polymer Solutions

Consider now the case of diffusion of NAT fragments in a polymer solution. The factors governing transport phenomena in the case of diffusion of low molecular weight solutes in polymer solutions have been well studied in the literature (see Astarita and Mashelkar, 1977 for a survey). It has been shown conclusively that the macroscopic or bulk viscosity of the medium as measured by a viscometer is not indicative of resistance offered to diffusion of a solute. Indeed it has been conclusively shown that in spite of several orders of magnitude rise in the bulk viscosity of the solution, the diffusion coefficients remain practically of the same order of magnitude as those in the case of the solvent (Mashelkar and Soylu, 1974).

It is to be noted that the bulk viscosity of the polymer solution where contributions to the flow resistance are made by the long chain nature of the polymer will not represent the resistance to diffusive movement in polymer solutions. In fact, the translational movement of a polymer molecule will occur by consecutive jump displacement of the chain segments; each jump resulting in the exchange of position of a segment and the solvent molecule. The overall movement will thus depend upon the effective "microviscosity" of the polymer segment-solvent region. Therefore, the bulk viscosity will be an overestimate of the forces opposing movement of the chain segments.

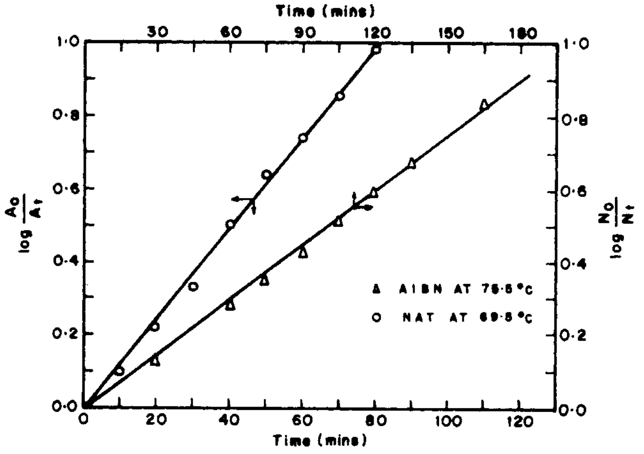


Figure 1. A typical first-order decomposition kinetics plot for decomposition of AIBN, and NAT in dimethyl formamide.

The term "microviscosity" has been consistently used in the literature, particularly for predicting transport phenomena in polymer solutions, especially molecular diffusion, electrical conduction etc. (Nishijima and Oster, 1956; Komiyama and Fuoss, 1972). Although this concept of microviscosity has been introduced for some time, no methods for its direct measurement have been reported in the literature. However, recently there have been some efforts to obtain this information. For example, Malinski and Zagorski (1979) used square wave polarography to determine microviscosity of aqueous dextran solutions.

Let us assume that the measure of resistance for diffusive movement in a macromolecular environment is provided by the microviscosity of the medium. If D_s and D denote the diffusivity of the solute in polymer solution and pure solvent, respectively, and η and η^* denote the solvent viscosity and the microviscosity of the polymer solution, we may assume that:

$$D\eta = D_s\eta^* \qquad (10)$$

Evaluation of η^* as defined above requires the knowledge of the ratio D_s/D and of η. It may indeed be assumed that the ratio of any other pertinent transport parameters in the place of D_s/D (such as electrical conductivities in pure solvent and polymer solution) may also be adequate to calculate the microviscosity. A good example of such an approach to calculate microviscosity is

TABLE 1. RATE CONSTANT FOR DECOMPOSITION OF AIBN

Medium	Temp. °C	$k \times 10^5$ s^{-1}
Polyethylene Glycol-200	81.8	20.21
	76.3	9.01
	69.3	3.72
Polyethylene Glycol-600	81.8	19.78
	76.3	9.09
	69.3	3.76
Polyethylene Glycol-1500	81.8	20.36
	76.3	9.16
	69.3	3.74
Dimethyl Formamide	76.3	8.55
4% Polyacrylonitrile Solution	76.3	8.31
1% Polyvinyl Alcohol Solution	76.3	8.31

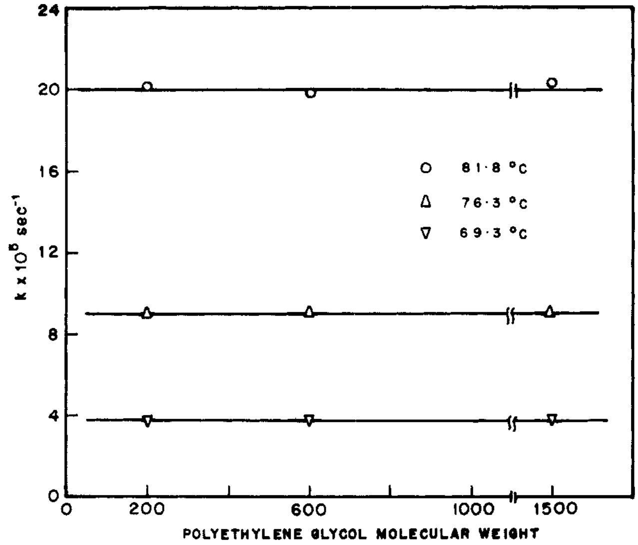


Figure 2. Dependence of decomposition constant of AIBN on polyethylene glycol molecular weight at various temperatures.

provided by Nishijima and Oster (1956), who studied diffusion of sucrose in polyvinyl pyrrolidone solutions and in pure solvents. The very recent work of Masszi et al. (1976), who used microwave dielectric method to examine the changes in dielectric parameters in polymer solutions and estimated the microviscosities independently is another case in point. Such measurements do indeed indicate that Eq. 10 above is a very adequate representation of the phenomenon.

In order to derive a predictive equation, we would take recourse to the existing theoretical models to predict the ratio D_s/D. Many such models exist in the literature (Navari et al., 1971; Li and Gainer, 1968; Osmers and Metzner, 1972), wherein the knowledge of physico-chemical properties enables one to calculate D_s/D. Such properties include unperturbed chain dimensions and solution constants of the polymer (Navari et al., 1971), heat of vaporisation (Li and Gainer, 1968), excess volume of mixing (Osmers and Metzner, 1972), etc. We will choose the model proposed by Li and Gainer (1968) to compute this ratio since it is simpler to use and is well tested against experimental data for its predictive ability. The model predicts that:

$$\frac{D_s}{D} = \left[\frac{M}{M_s}\right]^{1/2}\left[\frac{V_s}{V}\right]^{1/3}\left[1 - \frac{\Delta H_m}{\Delta H_{vap}}\right] \tag{11}$$

TABLE 2. RATE CONSTANTS FOR DECOMPOSITION OF NAT IN POLYETHYLENE GLYCOLS

Medium	Temp. °C	$k \times 10^5$ s^{-1}	η^* cP
Polyethylene Glycol-200	81.0	31.64	3.23
	75.5	16.18	3.56
	69.5	8.41	3.97
	65.0	4.99	—
Polyethylene Glycol-400	81.5	24.27	5.02
	75.5	14.06	5.38
	69.5	6.37	6.13
Polyethylene Glycol-600	81.0	21.59	5.41
	75.5	15.02	5.92
	69.5	6.44	6.65
	68.0	5.07	—
Polyethylene Glycol-1000	81.5	19.92	7.55
	75.5	12.18	8.09
	69.5	5.44	9.33
Polyethylene Glycol-1500	81.5	20.19	7.77
	75.5	12.83	8.78
	69.0	5.93	9.59

Here, M and M_s denote the molecular weights of the solvent and polymer solution, V and V_s denote the molar volumes of the solvent and polymer solution, ΔH_m denotes the heat of mixing of the polymer-solvent system and ΔH_{vap} denotes the molar heat of vaporization of pure solvent. All the quantities are easily calculated in an *a priori* manner. We then have:

$$\eta^* = \eta\left(\frac{M_s}{M}\right)^{1/2}\left(\frac{V}{V_s}\right)^{1/3}\left(1 - \frac{\Delta H_m}{\Delta H_{vap}}\right)^{-1} \tag{12}$$

Microviscosity of polymer solution at a given temperature and polymer concentration can thus be calculated from the knowledge of the appropriate physico-chemical constants of the solution.

Diffusion in Medium Viscosity System

Let us now consider the problem of diffusion of a low molecular weight solute (such as an NAT fragment) in media where the viscosity increase is caused by the addition of a medium molecular weight additive (such as glycerol or glycol). Literature review indicates that diffusivity in such systems varies inversely with viscosity raised to an exponent which is close to 2/3. In fact, the assumption of validity of Stokes-Einstein equation in such systems has at times led to irrational conclusions (Hasinoff, 1977). The exponent 2/3 has been recently justified on the basis of Eyring rate theory (Hiss and Cussler, 1973). From Eyring rate theory, we have:

$$\eta = \frac{h}{l^3}\exp\left(\frac{\Delta G^‡}{K\,T}\right) \tag{13}$$

and diffusion coefficient:

$$D = \frac{l^2 K\,T}{h}\exp\left(\frac{-\Delta G^‡}{K\,T}\right) \tag{14}$$

When solute and solvent molecules are comparable in size, l becomes a characteristic of solute diameter alone and we have:

$$D\eta = \frac{K\,T}{l} \tag{15}$$

On the contrary, when the solute (such as NAT fragment) is smaller than the solvent molecule, l becomes characteristic of the solvent and we have:

$$D\eta^{2/3} = K\,T\,h^{1/3}\exp(-\Delta G‡/3\,K\,T) \tag{16}$$

Validity of this relationship has been established in literature by various workers for diverse systems (Hikita et al., 1978; Calderbank, 1959; Hayduck and Malik, 1971; Yagi and Yoshida, 1975). In view of Eq. 16, following an argument similar to that in the case of polymer solution, we may deduce that:

$$\eta^* = \left(\frac{\eta_s}{\eta}\right)^{2/3}\eta \tag{17}$$

In summary then, we have a way of predicting microviscosity η^* in the case of ordinary low molecular weight low viscosity solvents ($\eta^* = \eta$), in the case of polymer solutions (Eq. 12), and also in case of medium viscosity solvents (Eq. 17). From Eq. 10 and Eq. 7 it follows that:

$$k_d\ \eta^* = \text{constant} \tag{18}$$

Thus, Eq. 8 can be rewritten as:

$$\frac{1}{k} = \frac{1}{k_1} + \frac{\eta^*}{\alpha} \tag{19}$$

A plot of $1/k$ vs. η^* should be linear. We can obtain $1/k_1$ as the intercept and $1/\alpha$ as the slope. Additionally, the variation of k_1 and k_d could be represented by Arrhenius equations of the type:

$$k_1 = A_1\ \exp-(\Delta E/RT) \tag{20}$$

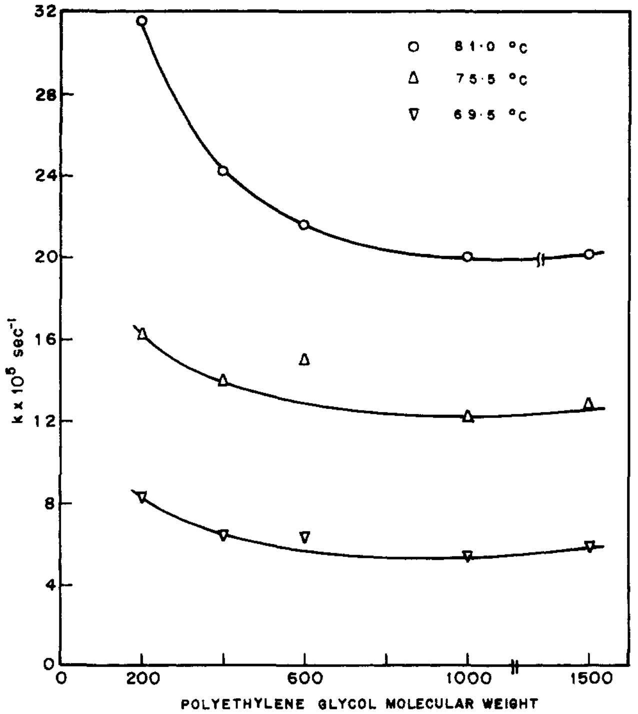


Figure 3. Dependence of decomposition constant of NAT on polyethylene glycol molecular weight at various temperatures.

$$k_{-1} = A_{-1} \exp(-\Delta E_{-1}/RT) \tag{21}$$

$$k_d = A_d \exp(-\Delta E_d/RT) \tag{22}$$

In the experimental investigation to follow, we shall evaluate some of the governing kinetic and diffusive parameters which emerge from the above theoretical analysis.

EXPERIMENTAL

Synthesis of NAT

Synthesis of NAT consisted of the following steps: (a) synthesis of p-nitrophenyl hydrazine; (b) synthesis of trityl chloride; (c) condensation of p-nitrophenyl hydrazine and trityl chloride; and (d) oxidation of the hydrazo precursor obtained in step (c) to NAT.

p-Nitrophenyl hydrazine was prepared by the method described in the literature (Fierz and Blangley, 1943). Trityl chloride was prepared according to the method described by Vogel (1975). The condensation of p-nitrophenyl hydrazine and trityl chloride was carried out as described by Cohen and Wang (1953) and the hydrazo precursor oxidized with isoamyl nitrite as described by Pryor and Smith (1970). Crude NAT was recrystallized from methanol. Purity of NAT was checked by thin layer chromatography and confirmed by elemental analysis. Melting point of the compound was determined and found to be 118-119°C.

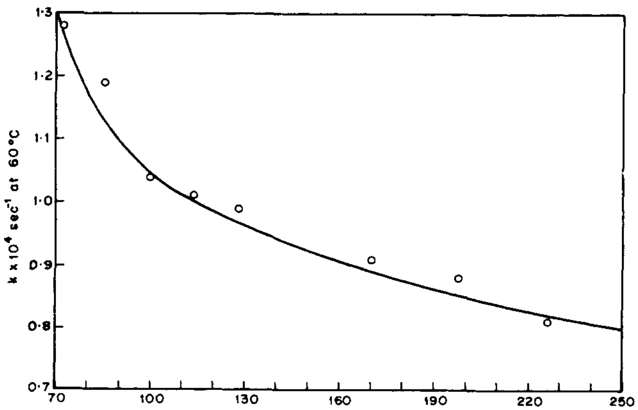


Figure 4. Dependence of decomposition constant of NAT on hydrocarbon molecular weight.

Purification of AIBN

AIBN was recrystallized twice from methanol. The compound melted with decomposition at 104°C.

Kinetics of Decomposition

Decomposition of AIBN was followed by the nitrogen evolution method described in detail in an earlier paper (Kulkarni et al., 1979).

Kinetics of decomposition of NAT was studied by following the decrease in absorbance at 22,000 cm^{-1} on a Specord UV-VIS spectrophotometer.

In this work, 70 sets of kinetic data with different systems have been taken and analyzed.

Characterization of Polyacrylonitrile

Polyacrylonitrile was characterized by dilute solution viscosity measurements in dimethylformamide at 25°C. The polymer had an intrinsic viscosity 1.27, which corresponds to the number average molecular weight 4.79 × 10^4 (Onyon, 1956).

Viscometry of Solutions

Viscosity of polymer solutions, polyethylene glycols and dimethyl formamide-glycerol blends was determined by using a concentric cylinder viscometer. Intrinsic viscosity of polyacrylonitrile solutions was determined on a Cannon-Fenske viscometer.

RESULTS AND DISCUSSION

Decomposition of AIBN

Decomposition of AIBN was confirmed to follow first-order kinetics. A typical plot (Figure 1) shows log N_0/N_t as a function of time. Here, N_0 and N_t represent number of moles of AIBN at zero time and at time t respectively.

Rate constants for decomposition of AIBN in polyethylene glycols of increasing molecular weights and in two polymer

TABLE 3. RATE CONSTANTS FOR DECOMPOSITION OF NAT IN DIMETHYL FORMAMIDE SOLUTIONS

Medium	Temp. °C	η* cP	$k \times 10^4$ s^{-1}
Dimethyl Formamide			
	69.5	0.70	2.13
	75.5	0.64	4.94
	80.0*	0.60	9.59
Dimethyl Formamide/Glycerol Blend (4/1)	69.0	0.93	1.79
	75.5	0.84	4.50
	80.0	0.78	—
Blend (3/2)			
	69.0	1.43	1.29
	75.5	1.28	3.05
	80.0	1.16	—
2% Polyacrylonitrile Solution in Dimethyl Formamide	69.5	1.25	2.19
	75.5	1.14	3.89
	80.0	1.07	7.75
4% Polyacrylonitrile Solution in Dimethyl Formamide			
	69.5	1.40	1.66
	75.5	1.28	3.65
	80.0	1.20	6.30
6% Polyacrylonitrile Solution in Dimethyl Formamide	69.5	1.51	1.23
	75.5	1.38	3.30
	80.0	1.29	5.59

* Extrapolated value from Arrhenius equation.

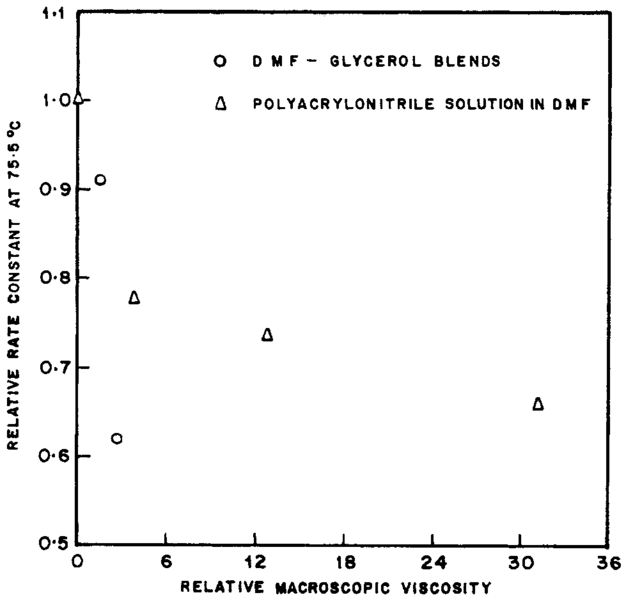


Figure. 5. Dependence of decomposition constant of NAT at 69.5°C in viscous media.

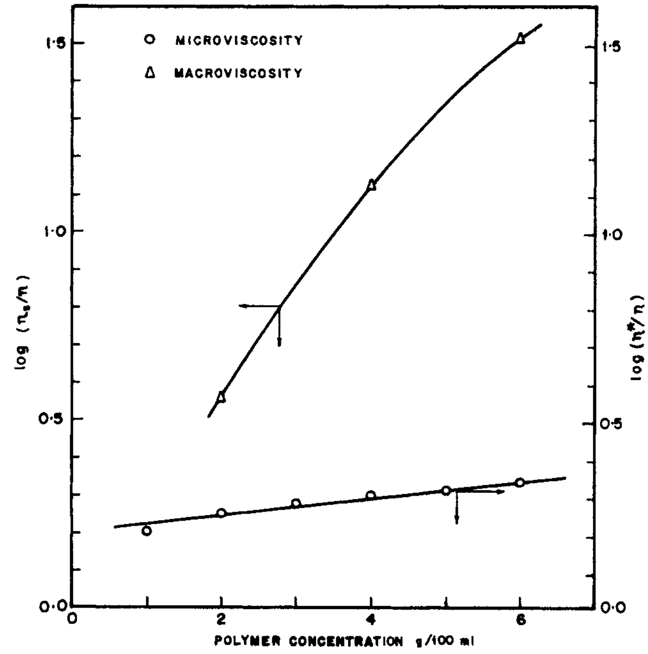


Figure 6. Relative viscosity of polyacrylonitrile solutions.

solutions are summarized in Table 1. The rate constant is independent of the molecular weight and hence the viscosity of the glycol can be seen from Figure 2. In the case of polymer solution, the rate constant is independent of the type of the polymer and polymer concentration. These findings are in agreement with earlier studies (Kulkarni et al., 1979; Deschrijver and Smets, 1966; Messerle et al., 1966). Since a nitrogen molecule is eliminated by simultaneous scission of two carbon-nitrogen bonds, any subsequent recombination of the fragments does not yield the parent molecule. Consequently, the decomposition constant is independent of the viscosity of the medium. This is also predicted by Eq. 5 for the case when $k_\beta >> k_d$.

Decomposition of NAT

Decomposition of NAT followed a first-order kinetics. A typical plot of log (A_0/A_t) where A_0 and A_t represent the absorbance at zero time and time t respectively is shown in Figure 1.

Rate constants for decomposition of NAT in polyethylene glycols are summarized in Table 2. A plot of decomposition constant vs. glycol molecular weight is shown in Figure 3. Comparison of Figure 2 and 3 clearly indicates that the dependence of decomposition constant of NAT on glycol molecular weight disappears above glycol molecular weight of 600. The behavior thereafter is similar to that of AIBN. Polyethylene glycols can be considered to be the precursors of polymer melts.

The results can be qualitatively explained by considering the number of carbon atoms constituting a segment, the motion of which enables the initiator fragment to diffuse through. The threshold value in this case appears to be in the vicinity of molecular weight of 600. An increase in the chain length of the polymer above this threshold value will have no effect on the diffusion of the fragments from the cage. These considerations are also supported by the work of Pryor and Smith (1970).

Figure 4 shows the dependence of decomposition constant of NAT on molecular weight of hydrocarbon. It is clear that there is a decrease in the decrement of rate constant with each carbon atom added to the hydrocarbon chain. It has been observed that such limiting behavior is observed not only with increasing chain length of the medium but also with increasing chain length of diffusant molecule as well. For example, diffusivity of alkanes in cis-polyisoprene tends to a limiting value as the number of carbon atoms in the diffusant molecule increases (Meerwall and Fergusson, 1979). Also, it has been observed that the energy of activation for diffusion of cetane in natural rubber is same as that of pentane (Chen and Ferry, 1968). The role of segmental motion in penetrant as well as substrate has been discussed by the authors elsewhere (Kulkarni and Mashelkar, 1980).

In order to further investigate the role of viscosity in the cage return process, the viscosity of solvent (DMF) was increased by the addition of glycerol and polyacrylonitrile. Pertinent kinetic data obtained are summarized in Table 3.

Unlike in the case of AIBN, which is an aliphatic azo compound, the solvent effects dominate the decomposition kinetics of aromatic azo compounds such as phenylazotriphenyl methane (Alder and Leffler, 1954). Although the variations are partly nullified by the compensation effect, significant differences are observed. It is not proposed to go into the details of solvation behavior of the ground and solvation states, but it is well established that the decomposition constant increases with an increase in the solubility parameter of the medium.

Based on similar considerations, it can be assumed that any increase in the solubility parameter of a medium would lead to an increase in the decomposition constant. Addition of glycerol (solubility parameter = 16.3) and polyacrylonitrile (solubility parameter = 12.35) should therefore lead to an increase in the decomposition constant, so far as the solvation considerations are concerned. The fact could not be verified experimentally since under experimental conditions NAT is only partly soluble in glycerol and polyacrylonitrile exists in a solid state.

A plot of the decomposition constant of NAT vs. viscosity of the medium is shown in Figure 5. It is seen that the decrement of rate constant for a given increment in viscosity of the solution is much greater for dimethyl formamide-glycerol system than that for the dimethyl formamide-polyacrylonitrile system. Such a behavior is to be expected on the basis of the analysis provided by us earlier. The microviscosities of solutions were calculated using Eq. 12 and 17. A plot of (η^*/η) for the system polyacrylonitrile-DMF is shown in Figure 6. For the purpose of comparison the ratio of (η_s/η) is also shown in the same figure. It is seen that inspite of the tremendous rise in macroscopic viscosity (η_s), the rise in microscopic viscosity (η^*) is small.

In order to test the validity of Eq. 10, we made a plot of $1/k$ vs. η^* for different systems (Figure 7). If the theoretical development was rational, the curve would be linear, and all the points will lie on a curve which is uniquely defined by the temperature and independent of the nature of viscogen. In other words, it is independent of whether the viscosity increment occurred due to addition of glycerol or polyacrylonitrile. This was indeed found

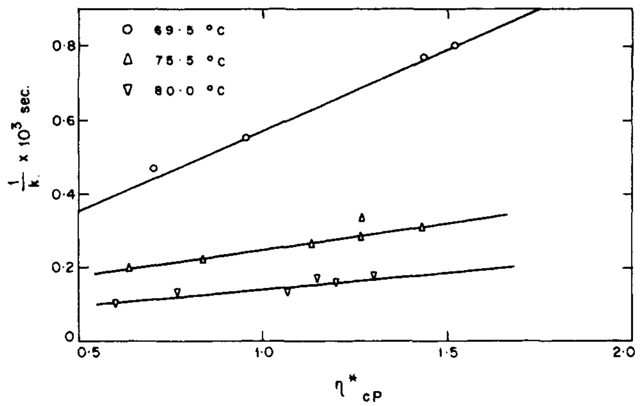


Figure 7. Plot of observed rate constant as a function of microviscosity of the medium at various temperatures.

TABLE 4. $\frac{k_{-1}}{k_d}$ VALUES FOR SYSTEMS INVESTIGATED

System	Temp. °C	$\frac{k_{-1}}{k_d}$
Dimethylformamide	69.5	0.66
	75.5	1.24
	80.5	2.06
Dimethylformamide/Glycerol Blend		
4/1	69.5	0.98
	75.5	1.46
	80.5	2.39
3/2	69.5	1.76
	75.5	2.63
	80.5	4.43
2% Polyacrylonitrile Solution in Dimethylformamide	69.5	0.62
	75.5	1.84
	80.5	2.78
4% Polyacrylonitrile Solution in Dimethylformamide	69.5	1.13
	75.5	2.03
	80.5	3.59
6% Polyacrylonitrile Solution in Dimethylformamide	69.5	1.89
	75.5	2.35
	80.5	4.24

to be the case. The value of $1/k_1$ was obtained by extrapolating down to $\eta^* = 0$.

We shall now investigate in further detail the way in which the system properties affect k_1, k_{-1} and k_d. Based on Eqs. 8 and 9 it is easily seen that the plot of $1/k$ against η^* gives $(k_{-1}/k_1\ 1/k_d)$ as the slope. Based on the plots made in Figure 7 these slopes were evaluated. The ratio k_{-1}/k_d was deduced by using the value of k_1 that was already determined. Table 4 shows these values for viscogens of different origins. It is interesting to note that the process of diffusive separation (represented by k_d) is as fast as the process of recombination (represented by k_{-1}). It is not possible to individually estimate the values of k_{-1} and k_d. However, an approximate order of magnitude estimate of k_d can be obtained by using Eq. 7. If we assume that the concentration of initiator 2×10^{-3} M, $R_1 = 15 \times 10^{-8}$ cm (estimated from known bond lengths) and $D = 10^{-5}$ cm^2/s, we obtain $k_d = 2.27 \times 10^7$ s^{-1}. This means that the process of diffusive separation is extremely rapid. This is intuitively obvious. It is reasonable to assume that the separation distance x, the diffusivity D and the time of separation t are correlated approximately by the relation $x = \sqrt{Dt}$. If we have $x \sim 10^{-6}$ cm (separation by approximately 6 to 7 molecular diameters), $D \sim 10^{-5}$ cm^2/s, it is seen that the time required for diffusive separation is of the order of 10^{-7}s. This is an extremely rapid process and in the present case the process of recombination competes with this diffusive separation process.

We shall now estimate the activation energies for different processes. The activation energy for decomposition reaction (k_1) was estimated by plotting ln k_1 vs. $1/T$ (see Figure 8). It was found that for DMF, we have ln A = 59.74 s^{-1} and $\Delta E_1 = 45.91$ kcal/mol.

As discussed in the earlier section on development of concept of microviscosity, the diffusion of a low molecular weight species in polymer solution is governed by the segmental motion of the polymer chain rather than the translational motion of the polymer chain as a whole. Since diffusivity as well as microviscosity are both governed by the segmental motion of the polymer chain, we can assume that the activation energy for diffusive process (k_d) is the same as that for the microviscosity η^*. Plots of η^* vs. $1/T$ were made and the resulting values of activation energies have been listed in Table 5. It is clearly seen that when glycerol is used as a viscogen, there is an increase in the activation energy. However, in the case of polymeric additive as a viscogen, the activation energy remains virtually the same. This is again intuitively obvious for any solvent dominated system (see Figure 6).

We shall now make an attempt to calculate the value of activation energy for the recombination process (k_{-1}). Figure 9 shows some typical Arrhenius plots. It must be emphasized here that due to want of sufficient data, generalized conclusions cannot be drawn. However, it would appear that the activation energy for recombination is in the region of 15 to 21 kcal/mol. In this connection it is interesting to compare the previous findings on activation energies for recombination process for simple radicals. Dobis et al. (1968) studied the recombination of CF_3 radicals in variety of solvents and observed that the recombination process had a negative activation energy. Our results are obviously in sharp contrast. One may only speculate that the recombination of CF_3 radicals may not involve a necessity of appropriate orientation of the radicals. Such orientation may

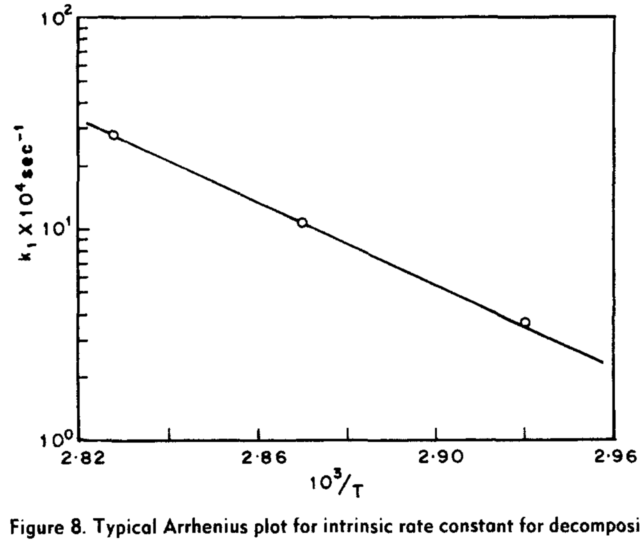


Figure 8. Typical Arrhenius plot for intrinsic rate constant for decomposition of NAT in viscous solutions.

TABLE 5. ENERGIES OF ACTIVATION FOR MICROVISCOSITY OF VISCOUS SOLUTIONS

	ΔE_r kcal/mol
Dimethylformamide	3.38
Dimethyl Formamide/Glycerol Blend	
4/1	3.81
3/2	4.66
2% Polyacrylonitrile Solution in Dimethylformamide	3.30
4% Polyacrylonitrile Solution in Dimethylformamide	3.38
6% Polyacrylonitrile Solution in Dimethylformamide	3.38

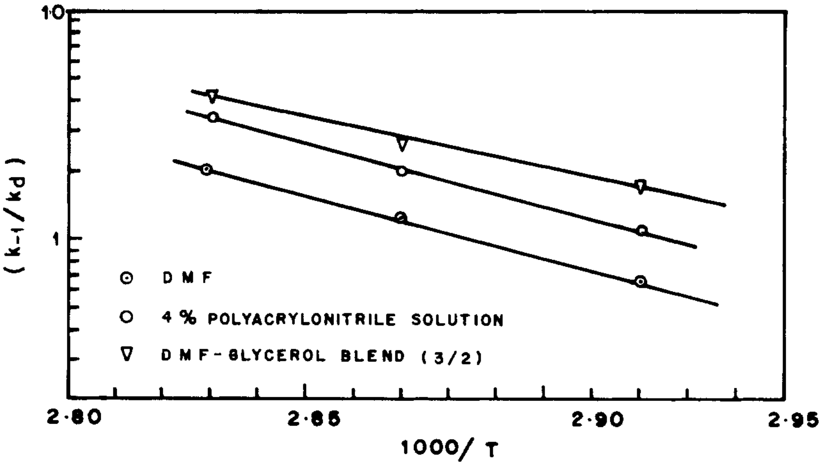


Figure 9. Arrhenius plot for the ratio of rate constants k_{-1}/k_d for typical systems.

play an important role in the case of bulky triphenylmethyl radicals investigated in this paper. Indeed an increase in temperature may increase the probability of combination of these radicals because the rotational diffusion constant may increase substantially.

As emphasized earlier, the introduction of the concept of microviscosity (η^*) enables us to obtain unique correlation of diffusive phenomena, which are unaffected by the nature of viscogen. We shall provide a simple test of this on the basis of our own experimental data. Fig. 10 shows the values of $(k_1/k_{-1})k_d\eta^*$ and $(k_1/k_{-1})k_d\eta_s$ for different systems plotted as a function of viscogen concentration at 75.5°C. We may assume that the ratio (k_1/k_{-1}) is independent of system properties. It can then be seen that the product $(k_1/k_{-1})k_d\eta^*$ remains constant for all the systems. However, the plots $(k_1/k_{-1})k_d\eta_s$ vs. viscogen concentration give an uncorrelated plot.

It is worth noting that the concept of "microviscosity" proposed in this work is somewhat akin to the concept of 'altered temperature' used by Osmers and Metzner (1972) to predict diffusivities in polymer solutions. According to their concept, addition of a polymer to a pure solvent will change the structure of the medium and therefore the diffusional resistance. The diffusion in a low molecular weight solute in such a structured medium can be considered to be equivalent to the diffusion of the same solute in pure solvent at an altered temperature. At that altered temperature the structure of the solution is the same as that of the polymer solution.

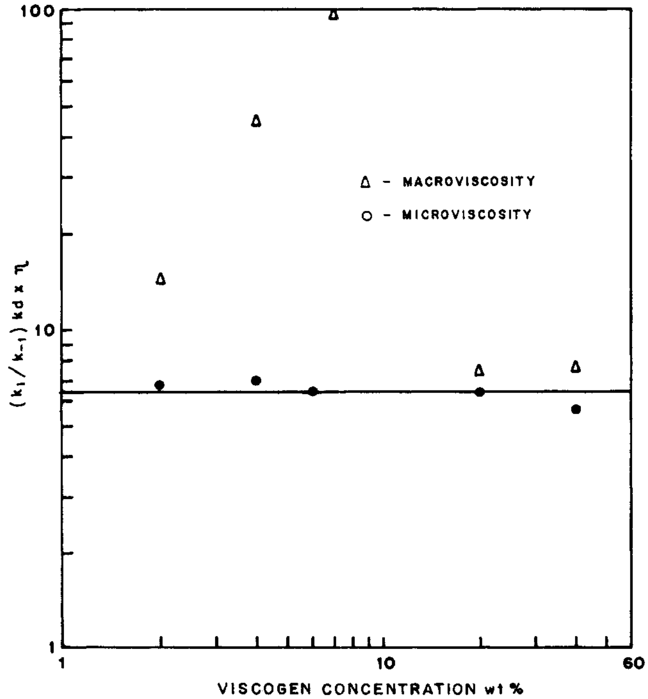


Figure 10. Dependence of the product $(k_1/k_{-1})k_d$ on viscogen concentration.

The physical concept proposed by us really envisages an assignment of an 'altered viscosity state' to the solvent, such that the effective diffusional resistance is the same as that offered by the structured medium obtained by polymer addition. The predictive equation given by us (Eq. 13) apparently offers an additional advantage in that all the physico-chemical parameters can be estimated in an *a priori* way. Indeed, the present approach can fruitfully be used for predicting other transport properties in polymer solutions, for example, electrical conduction. A preliminary analysis conducted on the basis of the literature data (for example, Wang, 1954; Komiyama and Fuoss, 1972) indicates that this may be a valid approach.

It is useful to indicate here that although diffusional effects play an important role in influencing the decomposition kinetics, hydrodynamics does not enter into the picture. Or in other words, the diffusive separation of fragments occurs on length scales which are too small in comparison to typical turbulence microscales. For instance, it can be seen that the diffusive separations occur over distances which are of the order of 10^{-8} cm (Allen and Patrick, 1974), which are considerably smaller in comparison to turbulence microscales which are of the order of 10^{-4} cm. Hydrodynamics will play a role, however, in the case described in our earlier paper (Kulkarni et al., 1979), where we discussed the process of decomposition of an initiator which was partially soluble in the medium (such as AIBN decomposition in DMF-glycerol medium). A similar situation is likely to arise in the case of DMF-glycerol blends containing higher proportions of glycerol than studied in this work, since NAT is only partly soluble in these media.

Our final comments concern the utility of the work presented here in polymerization reactor modelling. Consider, for instance, sulfochlorination of low density polyethylene (LDPE) to produce different grades of sulfochlorinated polyethylenes (sold commercially as Hypalon). The process is usually carried out by dissolving LDPE in carbon tetrachloride and bubbling chlorine and sulfur dioxide in the polymer solution consecutively. The decomposition process of a single bond initiator in a continuously changing macromolecular environment in such a system can be predicted easily with the help of limited data in the solvent system itself. Indeed a plot such as the one shown in Figure 10 enables us to calculate $\frac{k_1 k_d}{k_{-1}}$ after knowing the values of η^* calculated by the *a priori* methods presented in this paper.

NOTATION

A_d = Arrhenius factor for temperature dependence of the diffusion of initiator fragments out of the cage
A_v = Arrhenius factor for temperature dependence of the viscosity of medium
A_o = absorbance of NAT solution at zero time
A_t = absorbance of NAT solution at time t
D = diffusivity of the initiator fragment in pure solvent
D_s = diffusivity of the initiator fragment in polymer solution
ΔE_1 = energy of activation for temperature dependence of intrinsic rate constant for decomposition reaction
ΔE_{-1} = energy of activation for temperature dependence of intrinsic rate constant for recombination reaction
ΔE_d = energy of activation for temperature dependence of diffusivity of initiator fragments out of the cage
ΔE_v = energy of activation for temperature dependence of microviscosity of medium
$\Delta G^{\ddagger}$ = free energy difference in activated state theory
h = Planck's constant
ΔH_{vap} = molar heat of vaporization of the solvent
ΔH_m = heat of mixing of polymer solution
K = Boltzmann's constant
k = observed rate constant
k_1 = rate constant for bond scission (first step)
k_{-1} = rate constant for recombination (first step)
k_d = rate constant for diffusion of initiator fragments out of cage I
k_β = rate constant for β scission process
l = characteristic intermolecular distance
M = molecular weight of the solvent
M_s = molecular weight of the polymer solution
N = Avogadro number
N_o = number of moles of AIBN at zero time
N_t = number of moles of AIBN at time t
R = gas constant
R_1 = sum of radii of NAT fragments
T = temperature
t = time
V = molar volume of the solvent
V_s = molar volume of the polymer solution
x = minimum distance for separation of fragments

Greek Letters

α = constant (Eq. 8)
β = β scission process
η = viscosity of the solvent
η_s = viscosity of the solution on addition of viscogen
η^* = microviscosity of the medium

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