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Termination rate constant in butyl acrylate batch emulsion polymerization

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Summary

The kinetics of seeded batch emulsion polymerization of n-butyl acrylate (BA) have been investigated at 50°C using potassium persulfate (KPS) as the thermal initiator. The variations in the average number of radicals per particle ($\bar{n}$) and termination rate constant (k_t) have been determined as a function of conversion for particles of different sizes using established kinetic equations. Contrary to expectations, the values of $\bar{n}$ were found to be unusually high and the values of k_t were found to be very low for all the reactions studied. The high values of $\bar{n}$ are consistent with the low rates of termination. An explanation has been proposed for the low values of k_t based on preliminary computations of the energy barrier for rotation about the terminal C-C bond of the polymer chain end of polybutyl acrylate (PBA).

Introduction

Emulsion polymerization process can be described by three Intervals. In Interval I, the polymer particles are formed (nucleation) and grow in the presence of monomer droplets and, optionally, emulsifier. Interval II starts once the nucleation has ceased and the particles grow in the presence of the monomer droplets with the concentration of the monomer in the particles being approximately constant. Interval III is characterized by polymerization of the monomer present solely within the particles. A number of comprehensive reviews of emulsion polymerization can be found in the literature[1-3].

Kinetics of emulsion polymerization of monomers such as styrene(Sty)[4-8], vinyl chloride(VCl)[9], methyl methacrylate(MMA)[2,10] and vinyl acetate(VAc)[11] which result in polymers of relatively high glass transition temperatures have been extensively studied. Understanding of the change in $\bar{n}$ as a function of conversion, particle size etc. for these and other monomers has been achieved. In Interval II, Sty[1] and MMA[10] polymerizations have been described by Case II ($\bar{n}$=1/2) and Case III ($\bar{n}$>1/2) kinetics of the generalized Smith Ewart (S-E) theory whereas VCl[9,11] and VAc[11] have been described by Case I ($\bar{n}$<1/2) kinetics of the S-E theory.

At high conversions (Interval III), the translational mobility of the polymer radicals essentially ceases due to chain entanglements and/or because the reaction temperature approaches the T_G of the polymer/monomer mixture. The termination rate becomes dependent on the ability of the free radical chain end to achieve the conformational orientation to combine with another radical chain end: the process of segmental diffusion. Since the reaction between the free radicals has negligible activation energy, the process of termination is highly diffusion controlled[12-14]. This leads to an initial increase in the rate of polymerization and an increase $\bar{n}$. A knowledge of the change in $\bar{n}$ and k_t is important to control the rate of polymerization and molecular weight of the polymer formed.

The emulsion polymerization of acrylates which form polymers of very low glass transition temperatures (T_G < -50°C) such as BA or 2-ethyl hexyl acrylate has not been studied extensively. There are only two recent publications that deal with the kinetics of emulsion polymerization of BA[15,16]. In these systems, since the polymerization temperature is significantly above the T_G, we would expect high rates of termination at high conversions due to the high segmental diffusion. However, it was found that the k_t for BA at 50°C and at 60% conversion was very low [16] (750 $dm^3 mole^{-1} s^{-1}$). The $\bar{n}$ at this conversion was found to be very high (3 to 9). These findings are contrary to expectations. It is the intention of the present study to i) investigate the variation of the $\bar{n}$ and the k_t at different conversions during the polymerization of BA and ii) offer an explanation for the low values of k_t based on the flexibility of the chain end determined from energy barriers for rotation about the terminal C-C bond.

Experimental

The BA (Rohm and Haas, 50 ppm MEHQ) seed polymer was prepared by batch polymerization. The recipe used is shown in Table I. Aerosol MA-80 (American Cyanamid) and Aerosol OT-75 (American Cyanamid) were used as surfactants. In a reactor equipped with a pitched turbine blade, the surfactants, deionized water and the monomer were taken, purged with nitrogen and heated to 65°C. At this temperature, a solution of KPS in deionized water was added. A rapid rise in temperature was seen, which levelled off at 79°C. The bath temperature was held at 65°C for 2 hours, then it was raised to 83°C and was held for 1.5 hours. The agitation was maintained at 130 RPM throughout the reaction. The final solids was determined to be 19.5% for an overall conversion of 98.6%. The particle size of the seed latex was measured to be 74 nm by photon correlation spectroscopy on a Nicomp Model HN5-90 spectrometer equipped with an autocorrelator (Model TC-100).

Table I : Polymerization Recipes

Ingredient	**Seed**	**A**	**B**	**C**
Seed Latex(19.49%)	-	12.71	2.542	1.271
Deionized water	413.2	197.98	206.16	207.21
Aerosol OT-75(75%)	3.0	-	-	-
Aerosol MA-80(80%)	1.0	0.2	0.2	0.1
n-Butyl Acrylate	100.0	50.0	50.0	50.0
Deionized water	5.0	15.0	15.0	15.0
Potassium Persulfate	0.25	0.3	0.15	0.075

Seeded emulsion polymerizations of BA monomer were carried out at 50°C in a batch mode. The amounts of the seed polymer, surfactant and initiator were varied and are shown inTable I.The monomer was purified by distillation at reduced pressure between 45 and 55°C. Aerosol MA-80 was used as the sole stabilizing agent at very low concentrations (<0.072 wt% in water) to avoid new particle generation. KPS (Reagent, J.T.Baker) was used as the thermal initiator. The surfactant and the initiator were used as received.

Aerosol MA-80, deionized water and the seed latex were charged to a reactor. Nitrogen was bubbled through the mixture at 1000 ml/min. for 20 minutes and distilled BA monomer was added. Nitrogen flow was continued for 25 minutes after which the flow was changed to be above the liquid level. The reactor contents were heated to 50°C and the solution of KPS in deionized water, purged with nitrogen, was added. The agitation was maintained at 150 RPM and the temperature was maintained between 50 and 51°C.

Samples were taken at periodic intervals and quenched with about 2 g. of 0.06% hydroquinone solution. The solids content was determined gravimetrically and the conversion calculated.

Results and Discussion

1) Estimates of average number of radicals per particle (ñ)

Fig. 1 shows the conversion profiles for the three seeded polymerizations. The details of the three reactions are shown in Table II. The rate of polymerization was determined from the conversion vs. time curve and is plotted in Figure 2. All three curves show a region of constant rate between 15 and about 50% conversion. The slight scatter seen in the data in this region is probably due to the use of gravimetry for determining the conversion and the technique used for determining the average rate.

Despite the scatter, three distinct regions, one of approach to steady state, one of nearly constant rate and one of gradually decreasing rate are seen. The rate is seen to decrease with the decrease in the number of seed particles. The experimentally determined rate was used to calculate ñ using the generalized S-E rate equation[1] :

$$R_p = k_p \cdot [M]_p \cdot \tilde{n} \cdot N/N_A \qquad (1)$$

where R_p is the rate of polymerization (mole dm^{-3} of H_2O. s^{-1}), k_p is the propagation rate constant (dm^3 of org. $mole^{-1}s^{-1}$), $[M]_p$ is the concentration of monomer in the particles (moles dm^{-3} of org.), N is the number of seed particles per dm^3 of water and N_A is the Avagadro number. For the calculation of ñ, the values for k_p and $[M]_p$ are needed. The values of k_p reported in the literature[17,18] for BA are highly scattered. We have used the value of 450 dm^3 $mole^{-1}$ s^{-1} at 50°C as reported by Maxwell et. al.[16]

The value of $[M]_p$ was determined from Figure 2 from the intersection of the drop in rate and the

Table II : Details of seeded polymerizations

Run	N, 10^{-15} dm^{-3} H_2O	[I], 10^{+3} mole dm^{-3} H_2O	[S], 10^{+3} mole dm^{-3} H_2O	$[M]_P$ mole dm^{-3} org.	a_S^*, 10^{-8} cm^2mole^{-1}	P.Dia. in nm. at 100% Conv.
A	50.16	4.98	1.85	3.05	47.13	206
B	10.00	2.49	1.85	3.40	9.40	348
C	5.02	1.25	0.93	3.60	9.43	437

* a_S = surface area of seed particles/ mole of surfactant

[S] = surfactant concentration

Table IV : Calculated k_t's for Run A

Av. Time, min.	Av. Rate, 10^{+4} mole dm^{-3} H_2O. s^{-1}	Conversion, %	$[M]_P$ mole dm^{-3} org.	$\bar{n}$ (Eq. 1)	a (Eq.3)	k_t, 10^{-3} dm^3 org. $mole^{-1}s^{-1}$
07.63	5.90	12.74	3.05	5.17	20.57	0.77
12.50	6.44	23.07	3.05	5.63	22.46	1.03
19.92	6.66	35.25	3.05	5.83	23.22	1.38
28.50	6.38	57.15	3.05	5.58	22.23	2.32
34.25	3.87	66.93	2.39	4.32	17.15	4.11
41.25	2.60	74.58	1.86	3.73	14.78	5.47
48.00	2.36	80.36	1.45	4.34	17.26	3.97

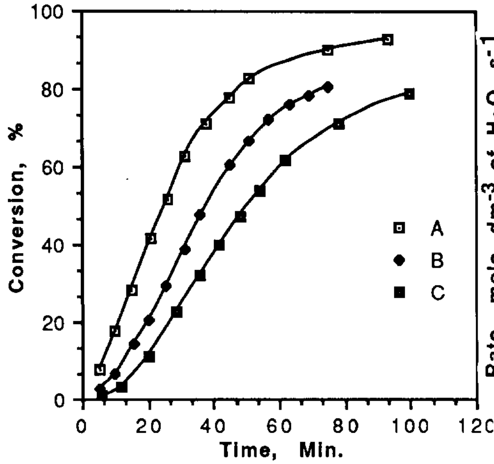

Fig. 1. Plot of conversion vs. time

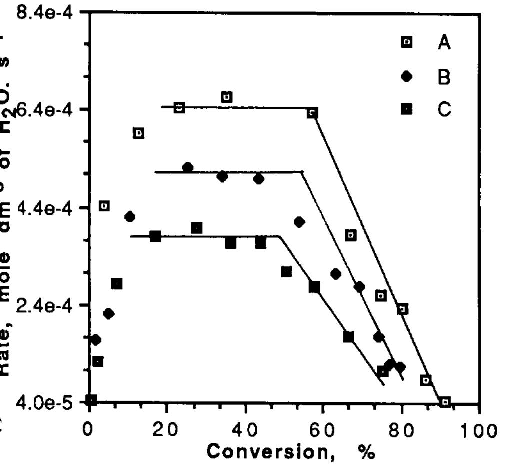

Fig. 2. Rate of polymn. vs. conversion

steady state value. This point corresponds to the disappearance of monomer droplets and represents the transition from Interval II to Interval III. The conversions at which the transition occured were found to be 57%, 54% and 50% for A, B and C respectively. The values of the monomer concentration in the particles corresponding to these conversions are shown in Table III. The monomer concentrations are seen to be slightly different for the three polymerizations. This is likely due to the differences in the adsorbed surfactant at the particle surface in the three reactions, leading to different degrees of swelling of the particles by the monomer. The individual monomer concentrations obtained have been used for the calculation of ñ for each reaction. These concentrations are lower than the 4.5 mole dm^{-3} obtained from equilibrium swelling measurements for BA by Capek et. al.[15] and are in the same range as reported by Maxwell et. al.[16] from kinetic measurements (3.1 - 3.25 mole dm^{-3}).

The value of ñ calculated at each conversion has been plotted in Figure 3. Because of the larger errors incurred in the calculation of the rate at low and high conversions, ñ as well as k_t has been calculated only at intermediate conversions. With decreasing amount of seed (increasing particle size), ñ is seen to increase. The system is also seen to have an unusually large ñ. This is unexpected for a polymer that has a very low T_G (-54°C) and is being synthesized 100°C above the T_G. The values of ñ of about 5 to 6 in Interval II for A correspond fairly well with the ñ values of 3 to 9 obtained by Maxwell et. al.[24] at lower initiator concentrations and at 60% conversion. The final particle radius in their case was much smaller, 70 nm as compared to theoretical radii of 103 nm, 174 nm, and 219 nm at 100% conversion for A, B and C respectively. This corresponds to an increase in the volume by a factor of 4.8 for B and by a factor of 9.6 for C over that of A. Correspondingly, the ñ values increase by a factor of about 3.5 for B and by a factor of 5 for C over that of A. The rate and consequently the average number of radicals per particle do not exhibit an increase in Interval III.

The general solution of the Smith-Ewart equation as presented by Stockmayer in the absence of desorption is[1]:

$$\tilde{n} = I_o(a)/I_1(a) \qquad (2)$$

where I_o and I_1 are Bessel functions of the first kind, and

$$a = \sqrt{8\alpha} \qquad (3)$$

$$\alpha = \rho_A \cdot v/N \cdot k_t \qquad (4)$$

$$\rho_A = f \cdot 2 \cdot k_d\,[I] \qquad (5)$$

where ρ_A is the rate of absorption of radicals into particles, v is the swollen volume of the particle in dm^3, k_t is in dm^3 org. $mole^{-1}s^{-1}$, f is the radical capture efficiency, k_d is the rate constant for initiator decomposition in s^{-1} and [I] is the initiator concentration in moles dm^{-3} of water .

Ugelstad and Mork[9] have suggested a very simple expression for ñ,

$$\tilde{n} = (0.25 + \alpha/2)^{1/2} \qquad (6)$$

where α has been defined above. They have shown this equation to be very comparable to the Stockmayer equation even at high values of $\tilde{n}$. From a knowledge of $\tilde{n}$ determined experimentally, using equation (6), α can be calculated. Combining equations (4) and (5) and using a determined from equation (6), k_t can be calculated. This Ugelstad and Mork equation has been used here to determine the value of k_t. It should be noted that some uncertainties in the calculated value of $[M]_p$ may slightly alter the values of $\tilde{n}$ and k_t but the validity of the conclusions are not affected.

2) Estimates of Radical Desorption Rates

To justify the use of Equations (1) through (6) we have to show first that the radical desorption rates, leading to more complex kinetics, are negligible. In the present system, it is reasonable to assume that desorption is minimal because of the following reasons: The rate of diffusion is known to drop sharply with chain length and we can assume that only single unit radicals can desorb from polymer particles.[1] As the rate of propagation for BA is very high, single unit radicals exist as such for very short times. The water solubilities and the transfer constants to monomer of a few of the monomers of interest have been listed in Table III[16,19,20]. From the Table we can see that the water solubility of BA is significantly lower than that of monomers such as VCl or VAc which are known to give radicals with high rates of desorption[11]. The transfer constant of polymer to BA monomer is not available in the literature. For purposes of comparison, the value of butyl methacrylate can be taken to be very close to that of BA. This is a reasonable assumption since the values for ethyl acrylate and ethyl methacrylate as well as methyl acrylate and MMA[20] are very similar. The transfer constants are significantly lower than those of VAc or VCl. Because of the lower transfer constant, lower water solubility and high k_p, the rate of desorption from particles is expected to be very low for BA.

Table III : Water solubilities and transfer constants of some monomers

Monomer	Solubility, wt.%	T,°C	$k_{tr,M}/k_p$	Ref.
Styrene	0.036	45	$0.35 \cdot 10^{-4}$	16,20
n-Butyl Acrylate	0.08	50		16
Butyl Methacrylate			$0.54 \cdot 10^{-4}$	20
Vinyl Chloride	0.6-1.06%	50	$6.4\text{-}13.5 \cdot 10^{-4}$	19,20
Vinyl Acetate	2.5	28	$0.25\text{-}20 \cdot 10^{-4}$	19,20
Methyl Acrylate			$0.275 \cdot 10^{-4}$	20
Methyl Methacrylate			$0.1\text{-}0.85 \cdot 10^{-4}$	20
Ethyl Acrylate			$0.193 \cdot 10^{-4}$	20
Ethyl Methacrylate			$0.259 \cdot 10^{-4}$	20

$k_{tr,M}/k_p$ = transfer constant of polymer to monomer

The rates of desorption for several monomers of different water solubilities can be calculated using Nomura's equation for the rate coefficient for radical desorption (k):[11,16]

$$k = (3zD_w/r_s^2)(k_{tr,M}/k_p)([M]_{aq}/[M]_p) \qquad (7)$$

where z has a value that ranges from zero to the maximum degree of polymerization of the exiting free radical, D_w is the diffusion coefficient of the free radical in water, r_s is the swollen radius of the particle, $k_{tr,M}/k_p$ is the transfer constant to monomer and $[M]_{aq}$ is the aqueous concentration of monomer. Taking the radius of swollen particle as 103 nm and assuming that the unit radical is the desorbing entity (z = 1) and using a value of D_w of 10^{-10} $m^2 s^{-1}$ for BA and Sty[16,21] and a value of $1.9 \cdot 10^{-9}$ $m^2 s^{-1}$ for VAc[11], the values of k for the three monomers can be theoretically calculated. The values predicted are $2.7 \cdot 10^{-3}$ s^{-1} for BA, $0.7 \cdot 10^{-3}$ s^{-1} for Sty and 17.5 s^{-1} for VAc using transfer constants of $5.4 \cdot 10^{-5}$, $3.5 \cdot 10^{-5}$, $10 \cdot 10^{-4}$ and $[M]_p$ of 3.4, 5 and 8.9 mole dm^{-3} respectively. In emulsion polymerization of Sty, desorption of radicals from the particles is taken to be negligible.[22] Since k for

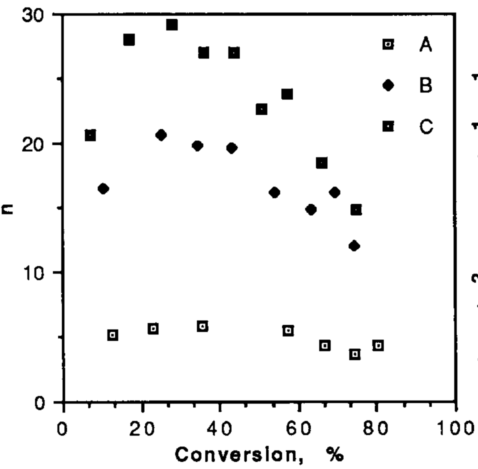

Fig. 3. ñ vs. conversion

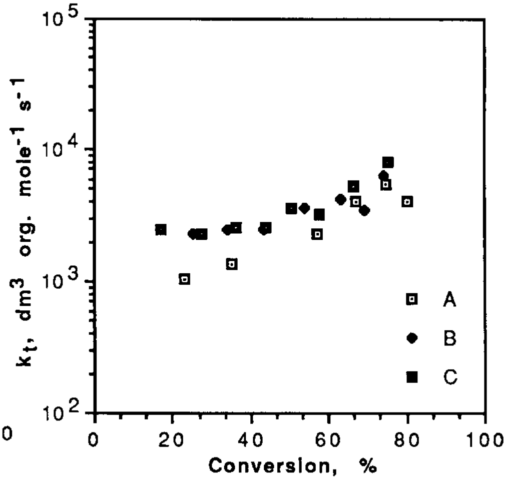

Fig. 4. Variation of kt with conversion

BA is comparable to that of Sty, we can assume radical desorption in BA systems to be minimal. Thus the use of equation (7) to calculate α and subsequently k_t should be reasonably accurate.

3) Estimates of the Termination Rate Constant

Table IV shows the calculated values of "a," v and k_t as a function of conversion for one of the reactions. The value of k_d was taken from Kolthoff and Miller[23] to be $1.45 \cdot 10^{-6}$ s^{-1} at 50°C and a pH = 7. The plot of k_t versus conversion for the three reactions is shown in Figure 4. Due to the higher degree of uncertainty in the calculation of the rate at low and high conversions, k_t values calculated only at intermediate conversions have been plotted in reactions with higher number of seed particles.

The initiator concentration for the three experiments ranged from $1.245 \cdot 10^{-3}$ to $4.98 \cdot 10^{-3}$ mole dm^{-3} H_2O. Maxwell et. al.[16] have determined the radical capture efficiency to be about 30% when the initiator concentration is about $1.4 \cdot 10^{-3}$ mol dm^{-3}. In their system, this efficiency is for the entry rate taking into account both radical generation from initiator decomposition and readsorption of desorbed radicals. In our calculations, the desorption and subsequent readsorption of radicals has not been considered as this would be expected to be negligible. We have used the capture efficiency of Maxwell et. al. as the efficiency for capture of radicals generated in the aqueous phase due to decomposition of the thermal initiator. Since we are not accounting for the readsorption of radicals, our values of the rate of radical adsorption may be slightly lower than actual, and the values of k_t calculated may thus be slightly lower than expected. However, it is seen from the data of Maxwell et. al.[16] that the capture efficiency goes down as the radical flux increases. Therefore, although our values of k_t may not be exact, they should be very close. For all the three experiments, the value of k_t is seen to range from about 1000 to about 5000 dm^3 org. $mole^{-1}$ s^{-1}. This is in good agreement with the value of 750 dm^3 org. $mole^{-1}$ s^{-1} obtained by Maxwell et. al.[16] at 50°C. It also compares well with the values obtained by Benson and North[12] ranging from about 1000 to 10000 dm^3 $mole^{-1}s^{-1}$ at higher solvent viscosities (> 0.01 Pa.s) at 30°C. However, these values of k_t are several orders of magnitude lower than those of Sty ($11.5 \cdot 10^7$ dm^3 $mole^{-1}s^{-1}$) and MMA ($2.4 \cdot 10^7$ dm^3 $mole^{-1}s^{-1}$) at 50°C.[20]

The plot of k_t versus conversion in Figure 4 appears to indicate a slight positive slope. In the calculation of k_t, we have assumed that the capture efficiency is constant all through the conversion for a given initiator concentration. Since we are using an ionic initiator, we would expect the number of ionic groups to increase at the particle surface as the reaction progresses by capture of ionic oligomeric radical species. Due to the increased surface charge density, there may actually be a reduction in the rate of capture of the radical species as the reaction progresses due to increased repulsive forces between the particle surface and the ionic oligomeric radicals. The fact that we are not accounting for this reduction in capture efficiency with conversion may be leading to the slight positive slope in Fig. 4.

The termination reaction between two polymer radicals can be regarded as a three stage process.[12,14] First, the radicals should gain proximity by translational diffusion. Secondly, they should assume a certain favourable configuration to come close enough to make contact. Finally, they should overcome the barrier for chemical reaction. It is quite reasonable to assume that the activation energy for chemical reaction between two radicals is negligible.[12]

Benson and North[12] found that the solution polymerization of BA becomes diffusion controlled at relatively low conversions. In seeded emulsion polymerization of BA, the weight fraction of polymer in the particles is very high from the beginning (> 50%). Hence we could expect the chains to be highly entangled and the center of mass diffusion to be unimportant in determining the value of k_t. Under these conditions, the active chain end diffuses by "reaction diffusion"[24] by virtue of its propagational growth. This is also described as "residual termination"[25] or "roving head diffusion".[14]

"A theory for the termination rate coefficient in high-conversion free-radical polymerization systems, based on the concept of chain-end diffusion by propagational growth" has been proposed by Russel et al.[14] This model based on residual termination, gives lower and upper bounds for k_t based on polymer chain properties. The lower bound of k_t is applicable for rigid chains and the upper bound is applicable for flexible chains. Although this model will have a wide range of application especially in high conversion polymerization systems, the real success in using this model depends on how well one can predict the "flexibilty" of the active polymer chain end.

If PBA is described as "flexible" due to its low glass transition temperature (-55°C) and Polymethyl methacrylate (PMMA) as "rigid" due to its high Tg (105°C), one would expect the k_t of PBA to approach that of the flexible chain limit and that of PMMA to approach that of the rigid chain limit. However, the experimental values of PBA reported in this work and in the literature[12,14] approach that of the rigid chain limit for k_t. This could indicate that the active chain end of PBA is not sufficiently mobile to explore its entire configurational space between propagation steps. In other words, even though the PBA chain is "statically flexible" due to its low Tg compared to PMMA, it is "dynamically inflexible"[26] and the short time scale motions could be severly hindered due to high barriers to rotation (trans-gauche isomerization) because of the presence of bulky side groups. This argument was used by Russell et. al.[14] to explain the differences in the termination rate coefficents of PBA and PMMA systems, but they found it difficult to postulate the degree of flexibility of the polymer chain end.

In order to determine the flexibility of the polymer chain end, we have attempted to estimate the energy barrier (ΔE) for rotation about the terminal C-C bond in a PBA and a PMMA trimer by molecular mechanics calculations using Polygraf, a computer aided molecular design and simulation software from BioDesign, Inc. of Pasadena, CA.[27]

The results indicate that this energy barrier (ΔE) is about 9 Kcal mole^{-1} for PBA and about 6.7 Kcal mole^{-1} for PMMA. The difference in the energy barrier between PBA and PMMA is about 2.3 Kcal mole^{-1}. According to P.G. de Gennes[26], one important characteristic which defines "dynamic flexibility" is this energy barrier to rotation (ΔE). If ΔE is very small compared to thermal energy, trans-gauche isomerisation can take place in times of about 10^{-11} s. The chain then is said to be "dynamically flexible". If ΔE is high, the time required for a transition between the two states (τ_p), called the persistence time, is given by:

$$\tau_p = \tau_o \exp(\Delta E/RT) \qquad (8)$$

Using equation (8) and the ΔE obtained from Polygraf, the ratio of the persistence times were calculated for PBA and PMMA. Assuming τ_o to be 10^{-11} s at 50°C, τ_p was calculated to be $1.2 \cdot 10^{-5}$ s for PBA and $3.4 \cdot 10^{-7}$ s for PMMA. It should be realized that the value of τ_p for PBA would be about two orders of magnitude larger than that for PMMA regardless of the assumed value of τ_o. The PBA chain end would thus take a much longer time than PMMA to achieve the configuration to make contact with another chain end.

It can be concluded that at short time scales, the chain end of PBA is more "dynamically rigid" compared to PMMA, possibly due to the presence of bulky butyl side groups. This could explain the low

k_t values obtained for BA polymerizations in seeded emulsion systems.

Additional work on the determination of the energy barriers of rotation about the C-C bond of radical chain ends of higher molecular weight PMMA and PBA would shed more light on the mechanism of diffusion controlled termination processes and should be a good starting point for further research.

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