A Kinetic Study of Homogeneous Bulk Polymerization of Ethyl Methacrylate Initiated by Benzoyl Peroxide and an N, N' -dimethylaniline Redox Pair

Serap ŞENEL, Belma IŞIK-YÜRÜKSOY, Olgun GÜVEN

Hacettepe University, Department of Chemistry,

Beytepe, Ankara-TURKEY

The homogenous bulk polymerization of ethyl methacrylate (EMA) was studied using benzoyl peroxide (BPO) and an N,N'-dimethylaniline (DMA) redox pair with the dilatometric method. The half-order dependence of the polymerization rate upon both the BPO and DMA concentrations was obtained. The overall activation energy of the polymerization was found to be between 32.3-55.3 kJ/mole for different initial molar ratios of the redox pair. A retaring effect was observed at lower polymerization temperatures for low concentrations of BPO. The formation of reddish colored polymers at higher DMA concentrations was explained by the adsorption of adduct formed between DMA radicals.

Introduction

Redox polymerization has the advantages of very short induction time, low activation energy 40-85 kJ/mole), production of high molecular weight polymers with high yields, ease of control of the polymerization reaction at low temperatures due to reduction of the side reactions, and the direct experimental proof of the transient radical intermediates. Many redox pairs containing organic and inorganic components have been used and well demonstrated in the literature[1-5]. Peroxides, persulphates, permanganates, etc. are used as oxidants and the salts of such metals as $Fe^{2+}, Cr^{2+}, Co^{2+}$ and hydroxyacids are the typical reducing agents used in these studies. Benzoyl peroxide (BPO) and an N,N'- dimethylaniline (DMA) system is an ideal redox pair for use in the polymerization of vinyl monomers. A detailed kinetic investigation of styrene polymerization was carried out at the relatively high temperatures of 30-60° C[6,7]. A comprehensive survey of redox systems used in the polymerization of vinyl monomers can be found in the review paper of Misra and Bajpaı[8].

In this study a BPO-DMA system was used to initiate the homogeneous bulk polymerization of ethyl methacrylate at low temperatures of 12-35°C. One of the interesting aspects of using this pair was the discoloration of the poly (ethyl methacrylate) obtained. A detailed kinetic investigation of this system was undertaken for various compositions and temperatures.

Experimental

Ethyl methacrylate (Merck) was stabilized with 15 ppm hydroquinone monoethyl ether. It was passed three times through a column filled with alumina (adsorption type). Before being used the monomer was further purified by vacuum distillation. N,N'-dimethylaniline, supplied by BDH Chemical Ltd. was used as received. Benzoyl peroxide, supplied by Fisher Scientific Company, was dissolved in chloroform, precipitated by using methanol, and then recrystallized[9].

The conversion curves were obtained by the dilatometric method. The results were also occasionally checked by the gravimetric method. The molecular weights of the resulting polymers were measured by the viscometric method (Ubbelohde-type viscometer) and were calculated by using the equation[10].

$$[\eta] = 15.49 \times 10^{-5} \cdot M_v^{0.679} \qquad dL/g \ (25°C; THF).$$

The characterization of the poly (ethylmethacrylate) (PEMA) samples obtained at various initiator-pair concentrations was also performed by recording the UV-VIS spectra of their THF solutions on a Philips PU-8715 UV-VIS spectrometer.

Results and Discussion

The first set of experiments was carried out at a fixed concentration of DMA, while the concentration of BPO was changed at a constant predetermined temperature. The concentration of DMA was 0.025 M, and that of BPO ranged between the limits 1.10×10^{-2} M and 1.62×10^{-1} M. Typical conversion-time plots are shown in Figure 1.

The effect of variations in concentrations of BPO on the parcentage of conversion is given in this figure. The percentage of conversion steadily increased with increasing BPO concentration, which was expected.

The typical rate expression for the radicalic polymerization initiated by a redox pair is given by the following equation:
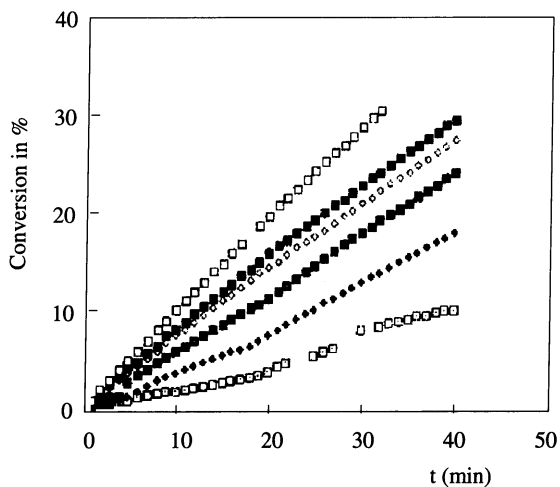

Figure 1. Conversion-time plot obtained at 35° C for a fixed (0.025 M) concentration of DMA. [BPO]/[DMA], ⊡ : 0.44, ◆: 0.81, ■: 1.16 ◇: 3.00, ■: 4.00,□: 6.50
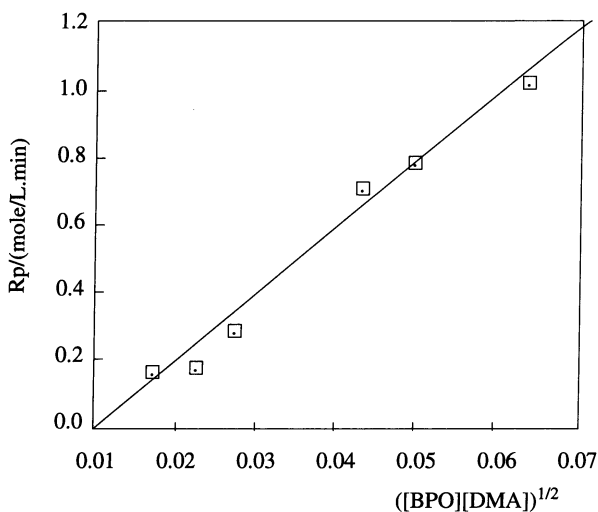
Figure 2. Effect of BPO and DMA concentration change upon polymerization rate at 35° C

$$R_p = \frac{k_p}{k_t^{1/2}}(fk_d[I])^{1/2}[M].$$

The dependence of the rate of polymerization on initator concentration is shown in Figure 2. The rate of polymerization as determined at 1% conversion exhibits a half-power dependence both on BPO and DMA concentrations, as can be seen in this figure. Therefore, the rate of polymerization is expressed by the following relationship

$$R_p \alpha [[BPO] \times [DMA]]^{1/2},$$

which is consistent with a bimolecular radical formation reaction.

These experiments were repeated at four temperatures (12, 18, 25, 35° C). The effect of temperature on the percentage of conversion is shown in Figure 3.
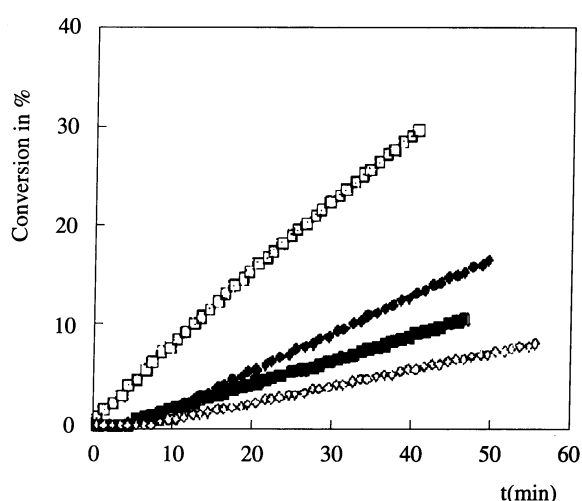

Figure 3. The effect of temperature upon conversion for the fixed value of 4.00 for [BPO]/[DMA] ratio. □:35, ♦:25, ■:18, ◇: 12° C
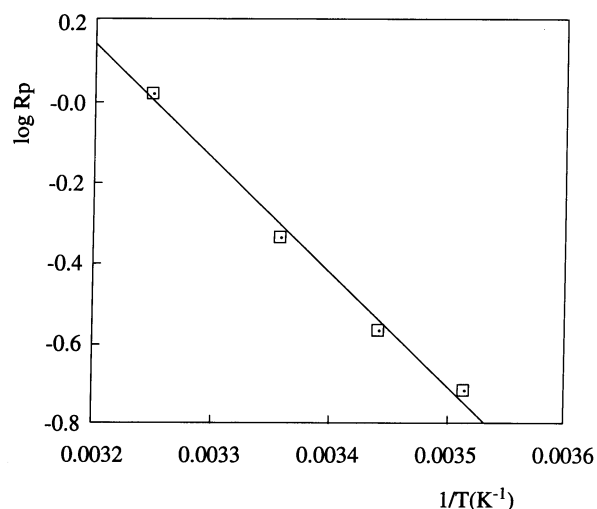
Figure 4. An Arrhenius plot for the value of 2.34 for [BPO]/ [DMA] ratio

The typical effect of enhancement in the rate of polymerization with increasing temperature is seen in this figure. The activation energy of the polymerization ranged between 32.3 and 55.3 kJ/mole for a redox pair ratio of 0.44 and 6.50, respectively. A typical Arrhenius plot is shown in Figure 4. The overall activation energy of the polymerization determined from this figure is 55.3 kJ/mole, for a redox pair ratio ([BPO]/[DMA]) of 6.50.

Before a discussion of the effects of other variables, such as temperature, initiator concentration, etc. on the kinetics of polymerization, it will be useful to consider the average molecular weights of the polymers obtained in this work. The viscosity's average molecular weights of the resulting polymers for three representative initiator concentrations are given in Table 1, together with the rates of polymerization as determined at various initiator-pair concentrations and temperatures.

Table 1. The change in M_v and rate of polymerization with respect to changes in temperature and redox-pair composition; [DMA]=0.025 M, constant
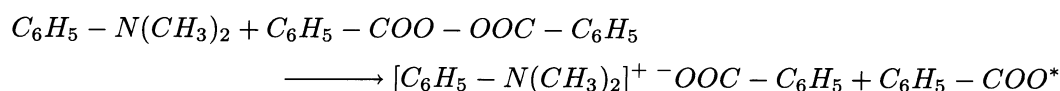
[BPO]/[DMA]	T(°C)	R_p(mole/L.min)	$M_v \times 10^{-3}$
0.44	12	-	-
	18	0.07	430
	25	0.11	390
	35	0.17	170
1.16	12	0.09	305
	18	0.13	300
	25	0.16	300
	35	0.30	-
6.50	12	0.19	105
	18	0.27	70
	25	0.47	-
	35	1.04	-

There are two general trends observed in Table 1: M_v decreases as the [BPO]/[DMA] ratio is increased at a constant temperature; and again a decrease in M_v is observed with increasing temperature at a constant initiator-pair concentration, where both are expected, i.e. when [BPO]/[DMA] ratio is increased for a constant DMA concentration at a fixed temperature). So the probability of ineffective consumption of benzoyl radicals by side reactions is increased. The polymerization temperatures used in this study were rather low compared with thermally-initiated polymerization. When benzoyl peroxide is used as one of the components of a redox pair, it does not decompose appreciably at the low polymerization temperatures of 18-35° C. Its presence in increased concentrations, however, can lead to its inductive decomposition by the growing chains. This will result in the formation of lower molecular weight polymers with peroxy end groups.

The above kinetic explanation for the synthesis of lower molecular weight polymers at higher [BPO]/[DMA] ratios was also confirmed by the observation of the peak at 1602 cm^{-1}. This corresponded to $C = C$ stretching of the aromatic ring, which originated from the BPO in the FTIR spectrum of the PEMA sample obtained from [BPO]/[DMA]=6.50, as given in Figure 5. For comparison purposes the IR spectrum of a PEMA sample obtained by gamma irradiation of its monomer is also included in this figure, together with the spectrum of BPO in the 1400-2000 cm^{-1} region.

M_v decreases as the temperature is increased at a constant [BPO]/[DMA] ratio. This is the general feature of temperature dependence of free radical polymerizations. The rate of polymerization is increased, and lower molecular weight products with wider molecular weight distributions are obtained with increasing temperatures. One of the interesting aspects of this study is that a retardation effect was observed when the temperature of polymerization was decreased. Either at 12 or 18° C, when the [BPO]/[DMA] ratio was lowered, the retardation period was observed to increase (Figure 6).

The reaction between DMA and BPO is not thoroughly understood, but in bulk polymerization proceeding to low conversions, it may be represented as a bimolecular decomposition that yields two types of free radicals[11], benzoyl and dimethylaniline radicals. The following reactions are the most probable pathways to the formation of these products:

$$C_6H_5 - N(CH_3)_2 + C_6H_5 - COO - OOC - C_6H_5$$
$$\longrightarrow [C_6H_5 - N(CH_3)_2]^+ \ ^-OOC - C_6H_5 + C_6H_5 - COO^*$$

$$[C_6H_5 - N(CH_3)_2]^+O^-OC - C_6H_5 \longrightarrow {}^*C_6H_5 - N(CH_3)_2 + C_6H_5 - COOH$$

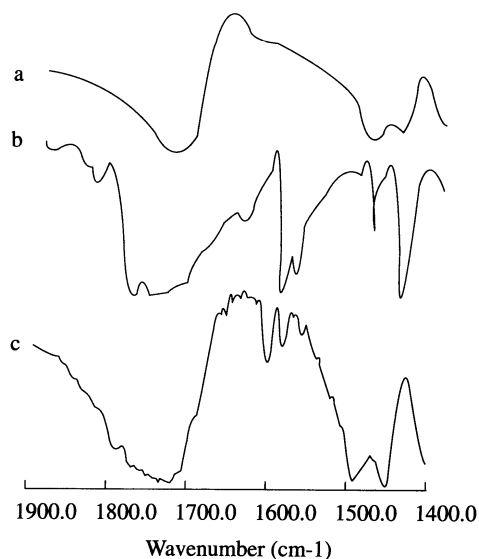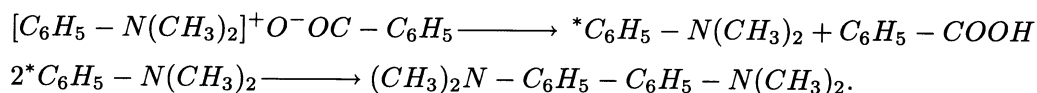$$2^*C_6H_5 - N(CH_3)_2 \longrightarrow (CH_3)_2N - C_6H_5 - C_6H_5 - N(CH_3)_2.$$

Figure 5. C=C stretching region of IR spectra of PEMA polymerized by gamma radiation (curve a), BPO (curve b), homopolymer sample synthesized at 18°C with a [BPO]/[DMA] ratio of 6.50 (curve c)
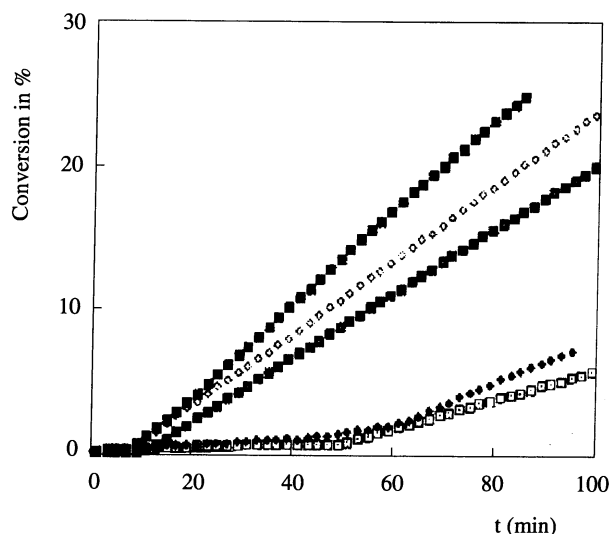
Figure 6. Conversion-time plot obtained at 18°C for a fixed (0.025M) concentration of DMA.[BPO]/[DMA], □: 0,44 ◆: 1.16, ■: 3.00, ◇: 4.00, ■: 6.50

It has already been determined that the dimethylaniline radical does not initiate the polymerization[10]. This radical is stabilized by resonance, and the recombination of these radicals as suggested by the third step of the above given reaction scheme would be more likely to occur. The product of this step is a colored compound, and we observed that as the concentration of DMA was increased, the color of the polymers obtained was darkened. The reddish color of these samples was due to the adsorbed adduct products of the dimethylaniline radicals. When these colored PEMA samples were dissolved in THF and reprecipitated by methanol, white PEMA was obtained. The UV-VIS spectra of the colored PEMA, together with the reprecipitated sample as given in Figure 7, can be taken as an experimental proof of consumption of the dimethylaniline radicals, which are inactive in the polymerization process.
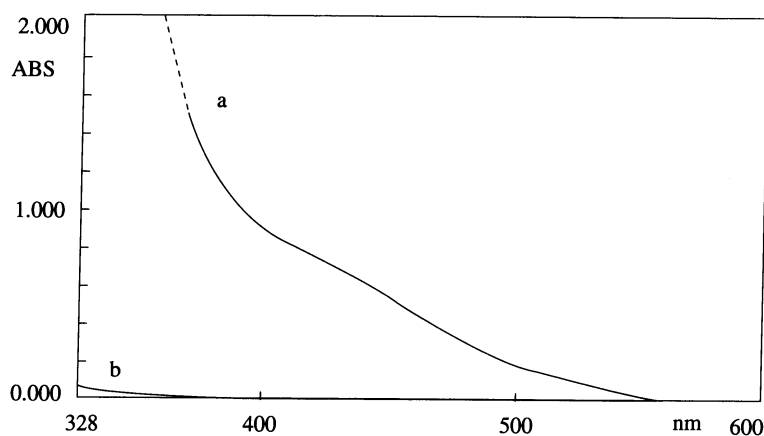
Figure 7. The UV-VIS spectra of colored PEMA in THF (curve a) and reprecipitated sample in THF (curve b)

It is therefore clear that the benzoyl radicals produced during the first step of the reactions given above are the precursors of the polymerization reaction.

In order to complete the kinetic analysis of bulk polymerization of EMA by the BPO/DMA redox pair, we attempted to explain the retardation observed at low temperatures and lower BPO concentrations. In order for a polymerization reaction to be detectable, the conversion must attain experimentally measurable quantities. This is obviously dependent on the availability of two active components in the reaction medium, namely monomer and free radicals. Since there is an excess amount of monomer in the system, it is not possible to get a significant amount of polymers before a certain concentration of free radicalic initiators is reached. The kinetics of radical formation for a BPO/DMA system in an apolar solvent, CCl_4, were followed. Figure 8 shows the change in the absorbance in the UV-VIS spectra of this mixture over time.

The temperature of the system was kept at 18° C, and the molar ratio of the redox pair was 1.16. A plot of absorbance recorded at 275.6 nm (a number we assigned due to the presence of the benzoyl radical) over time is given in Figure 9. The increase in the absorbance value, which corresponds to radical concentration, is almost identical in appearance to the polymerization rate curve given in Figure 6. This suggests that the retardation observed in the polymerization of EMA by the BPO/DMA pair is most probably due to very slow decomposition rates of the redox pair at low temperatures and low DMA concentrations.

In conclusion, we can say that a BPO/DMA redox system can be effectively used for the polymerization of ethylmethacrylate, with reliable control of the induction time and initation rate of the polymerization.
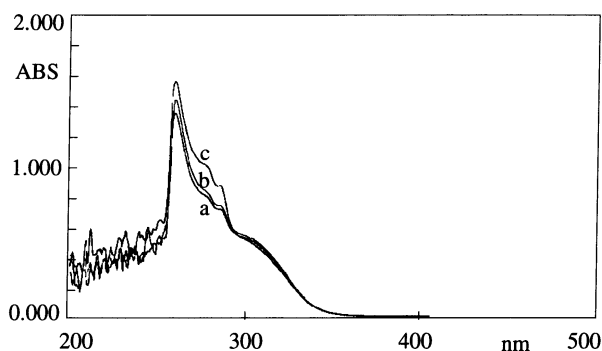

Figure 8. UV spectra of BPO-DMA mixture in CCl_4 at 18° C for 1.16 as [BPO]/[DMA] ratio at t=0, 75, 135 minutes (curves a,b,c)
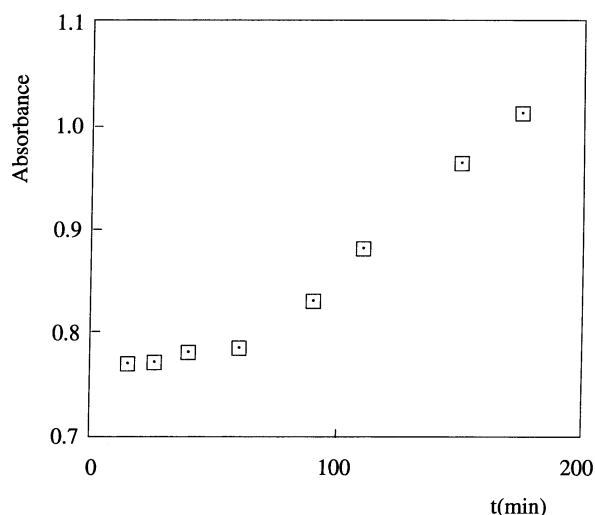
Figure 9. Absorbance-time plot for the BPO-DMA mixture in CCl_4 at 18° C for [BPO]/[DMA]=1.16 ratio recorded at 275.6 nm

References

1. G. S. Misra, C. V. Gupta, **Makromol. Chem.**, **156**, 195 (1972).

2. G. S. Misra, C. V. Gupta, **Makromol. Chem.**, **168**, 105 (1973).

3. G. S. Misra, J. J. Rabello, **Makromol. Chem.**, **175**, 3117 (1974).

4. M. Husain, S. N. Misra, **Makromol. Chem.**, **179**, 41 (1978).

5. E. Rizzardo, D. H. Solomon, **J. Macromol. Sci. -Chem.**, **A14(1)**, 33 (1980).

6. K. F. O'Driscoll, J. F. Schmidt, **J. Polym. Sci.**, **35**, 189 (1960).

7. K. F. O'Driscoll, S. A. Mc Ardle, **J. Polym. Sci., 40,** 557 (1959).

8. G. S. Misra, U. D. N. Bajpat, **Prog. Polym. Sci., 8,** 61 (1982).

9. M. Imoto, T. Otsu, K. Kimura, **J. Polym. Sci., 15,** 475 (1955).

10. G. Samay, M. Kubin, J. Podesva, **Angew. Makromol. Chem., 72,** 185 (1978).

11. K. J. Saunders, Organic Polymer Chemistry, Chapman and Hall, London, 211 (1973).