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Solvent effects on the free-radical polymerization of methyl methacrylate

M. Fernández-Garcia, J.J. Martinez and E.L. Madruga*
Instituto de Ciencia y Tecnologia de Polimeros (CSIC), Juan de la Cieva, 3.28006 Madrid, Spain
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The radical polymerization of methyl methacrylate has been studied in toluene and benzonitrile at 30, 45 and 60°C using 2-2' azobisisobutyronitrile as initiator. Under the conditions of our experiments both the rates of polymerization and the molecular weights of the polymer obtained are dependent on the nature of the solvent. Determination of the effective initiation rate and the coupled parameter $k_p/k_t^{1/2}$ (where k_p and k_t are the constants for propagation and termination reactions, respectively) show that the dependence of the rate of polymerization on the nature of solvent arises in part from the effects of viscosity, polymer chain extension and polymer chain lengths on the termination coefficient and in part from a dependence of the effective initiation rate on the nature of the solvent. © 1997 Elsevier Science Ltd.

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Introduction

Since relatively new experimental techniques[1-3] have emerged, increased interest has been generated in the variation of propagation and termination rate constant as a function of the experimental conditions. From these studies it is generally accepted that the termination rate constant, being diffusion controlled, is chain length dependent[4-7] whereas the propagation rate constant is usually considered to be independent of chain length. Notwithstanding, there is some evidence suggesting that the propagation rate constant is also chain length dependent, at least for the first few propagation steps[8-10]. A mechanistic interpretation of these results, however, is complicated[11]. In order to gain additional insight into elemental processes in free radical polymerization an understanding of solvent effect is of paramount importance. The solvent is known to influence not only polymer characteristic such as coil size and mobility but also many system properties such as viscosity and polarity.

Since the pioneering work of Burnett *et al.*[12], many publications have referred to solvent effects on the kinetics of the radical homopolymerization[13]. These studies have shown that the initiation rate is not affected by the presence of different solvents[14,15] and the termination rate appears to be proportional to the medium fluidity[14-19]. The small effect on the propagation rate constant has been attributed to complexing of the propagating radical with solvent[19-24]. However, besides the influence of the medium viscosity it has also been shown that solvent thermodynamic quality affects the termination rate coefficient[25]. On the contrary, the initiator efficiency factor will vary with the viscosity[26,27] and the rate coefficient for initiator decomposition could be affected by environment polarity[28,29]. Concerning the propagation step, recent papers found the propagation rate coefficient to be the same in bulk and in solution[30-33].

The aim of this paper is to examine solvent effects on the rate coefficients of methyl methacrylate homopolymerization. For purposes of consistency with several recent papers[33-35] toluene and benzonitrile were used as solvents.

When toluene is used a solvent Beuermann *et al.*[33,34] found that both propagation and termination rate constant are independent of the solvent whereas variations of both propagation and termination rate constant have been observed when benzonitrile is used as a solvent[14,35].

Most recent studies have used non-steady state methods to determine values of elemental kinetic coefficients disregarding the simple polymerization experiment, that is, the measure of steady-state rates of polymerization. However, the interpretation of experimental information regarding the variation of rate of polymerization, the effective rate coefficient for initiation and the $k_p/k_t^{1/2}$ (k_p and k_t being the propagation and termination rate constants, respectively) parameter as a function of the experimental conditions could shed new light on the free radical homopolymerization process. This investigation focuses on the steady-state free radical polymerization of methyl methacrylate in toluene and benzonitrile solutions.

Experimental Part

Materials. Methyl methacrylate (MMA) was purified by conventional methods[36].

2-2'-azobisisobutyronitrile (AIBN) was purified by successive crystallization from methanol.

Toluene (TO, Merk) for analysis was used without any further purification. Benzonitrile (BN, C. Erba) was purified using an appropriate chemical method[37]. The solvents were freshly distilled immediately prior to use.

2,2'-Diphenyl-1-picrylhydrazyl (DPPH, Fluka) was used without any further purification.

Polymerization. Polymerizations were carried out at 30, 45 and 60 ± 0.1°C in pyrex glass ampoules sealed off under high vacuum. Monomer and initiator concentration were 3 mol L^{-1} and 1.5 × 10^{-2} mol L^{-1}. After the designated time, the reaction mixture was transferred to a vessel and the contents poured into a large excess of methanol. The precipitated polymer was filtered and dried under vacuum until constant weight was reached. Monomer conversion was measured gravimetrically.

The rate of initiation was studied using the experimental
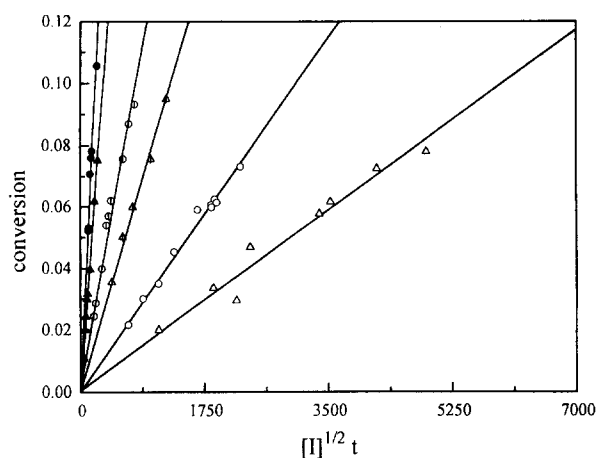
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* To whom correspondence should be addressed

Figure 1 Radical polymerization of MMA in 3 mol L^{-1} TO (Δ) and BN (O) solution. Polymerization Temperatures: 60°C, Solid points; 45°C, Scratch points and 30°C, Open points.
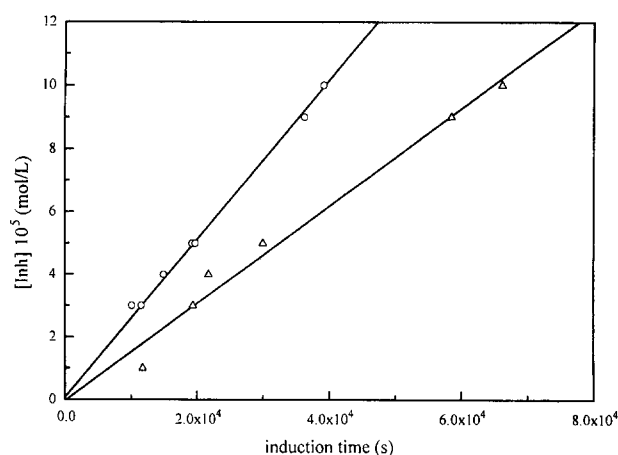

Figure 2 Determination of R_i in a 3 mol L^{-1} TO (Δ) and BN (O) solution at 30°C for MMA. [AIBN] = 1.5×10^{-2} mol L^{-1}.

conditions mentioned above at various concentrations of DPPH inhibitor.

Characterization. Intrinsic viscosities of poly(methyl methacrylate) in TO and BN were measured at 25°C with a Fica automatic viscometer. Molecular weights were determined with a Water Associates GPC equipped with a high-pressure solvent delivery system (Model 150) and a differential refractometer (Model R-401) operated at 25°C. Calibration of the instrument was performed with 14 standard samples of poly(methyl methacrylate) (Polymer

Laboratory LTD) with molecular weights in the range 1.4 $\times$ 10^6 and 3.0 $\times$ 10^3.

Results and discussion

Free radical polymerization of MMA have been carried out using 1.5×10^{-2} mol L^{-1} of AIBN as initiator in a 3 mol L^{-1} monomer solution of TO and BN. Overall polymerization and initiation rates, have been determined in different solvents at various temperatures, by gravimetry and by the inhibitor methods.

Figure 1 shows conversion versus time for various homopolymerizations. From this data it is possible to determine the overall homopolymerization parameter, K, based on the kinetic expression for homopolyization.

$$R_p = K[I]^{1/2}[M] \qquad (2)$$

where $[I]$ and $[M]$ are the initiator and monomer concentration. For K, we have

$$K = \frac{k_p}{k_t^{1/2}}(2fk_d)^{1/2}$$

where k_d, k_p and k_t are the constants for initiation, propagation and termination reactions, respectively and f is the efficiency factor.

The initiation rate R_i was determined by the inhibition method using DPPH as inhibitor

$$R_i = \frac{z_0}{t_i} \qquad (3)$$

where Z_0 and t_i are the concentration of inhibitor and the induction period, respectively.

Values of R_i were calculated from the slope of the plots such as that in *Figure 2*, which shows the concentration of DDPH as a function of the induction period. From the R_i obtained for the initiator concentration used in our experiments (1.5×10^{-2} mol L^{-1}) the effective rate coefficients for initiation, $2fk_d$ have been determined.

Once the initiator rate was determined, the ratio $k_p/k_t^{1/2}$ was evaluated from

$$\frac{K}{(2fk_d)^{1/2}} = \frac{k_p}{k_t^{1/1}} \qquad (4)$$

Values of K, $2fk_d$ and $k_p/k_t^{1/2}$ in the different solvents at the different polymerization temperatures are shown in *Table 1*.

Analysis of the reaction medium. Solvent quality and viscosity are the two factors normally introduced in discussing the effect of solvents on termination rate constants. Solvent quality increases the size of the solvated macromolecules[25], decreasing the rate constant of the termination reaction. An estimation of the size of solvated macromolecules in the reaction medium is given by the value of

Table 1 Solvent effects on the rate coefficients, number average molecular weight and polydispersity of poly(methyl methacrylate) obtained at various temperatures

Solvent	T (°C)	$K \times 10^5$ (mol$^{-1/2}$ L$^{1/2}$ s^{-1})	$2fk_d \times 10^6$ (s^{-1})	$k_p/k_t^{1/2} \times 10^2$ (mol$^{1/2}$ L$^{1/2}$ s$^{-1/2}$)	$\bar{M}_n \times 10^{-5}$ (g mol^{-1})	$\dfrac{\bar{M}_w}{\bar{M}_n}$
Toluene	30	1.70	0.10	5.38	6.95	2.1
	45	7.72	1.40	6.52	2.91	1.8
	60	29.77	11.25	8.88	1.12	1.9
Benzonitrile	30	3.26	0.17	7.91	7.92	2.1
	45	12.27	1.86	9.00	3.26	2.1
	60	47.13	20.20	10.49	1.77	1.8

the intrinsic viscosity, $[\eta]$. The intrinsic viscosity is related to the root-mean-square end-to-end distance, $(\bar{r}_0^2)^{1/2}$, by the equation

$$[\eta]\bar{M} = \phi(\bar{r}_0^2)^{3/2}$$

where M is the polymer molecular weight and ϕ the universal Flory constant. $[\eta]$ was measured at 25°C in each solvent and for poly(methyl methacrylate) M was 74 000. As can be seen in *Table 2* the size of macromolecules decrease in the order

$$BN > TO$$

From pure liquid viscosities for MMA[38] and the solvents[39], the solution viscosities, η_{mix}, of the reaction medium at 25°C have been calculated using the relationship[31,33]

$$\log(\eta_{mix}) = \chi_{MMA,0}\log(\eta_{MMA}) + (1 - \chi_{MMA,0})\log(\eta_{solv})$$

where $\chi_{MMA,0}$ is the monomer mole fraction of MMA and η_i is the viscosity of pure solvents.

Solution viscosities together with polarity of the solvents, which may influence the coefficient values for the initiator decomposition, are shown in *Table 2*.

Analysis of the rate coefficients. From data of *Table 1* it is clear that, independent of the solvent used, the overall homopolymerization parameter K increases with the polymerization temperature. The solvent effect causes methyl methacrylate to polymerise more rapidly in BN solutions. The temperature dependence for K is described by

$$K(mol^{-1/2} L^{1/2} s^{-1}) = 10^{9.05\pm0.10}$$

$$exp((-79.7 \pm 0.7 \, kJ \, mol^{-1})/RT)$$

for the homopolymerization of MMA in TO and

$$K(mol^{-1/2} L^{1/2} s^{-1}) = 10^{8.39\pm0.37}$$

$$exp((-74.4 \pm 2.2 \, kJ \, mol^{-1})/RT)$$

for the homopolymerization of MMA in BN.

The activation energies for the overall polymerization rate constants in TO and BN are in good agreement with the values found in free radical polymerization reactions[40].

The observed variation in the overall polymerization parameter could arise as a consequence of the variation of the effective rate coefficient for initiation and/or the variation of the coupled parameter $k_p/k_t^{1/2}$.

It can be seen from *Table 1* that the effective rate coefficient, $2fk_d$, is only weakly affected by the solvent. Values obtained in the different solvents increase in the order

$$TO < BN$$

Although the precise role of solvent in initiation remains

obscure and more than one effect may be involved, there is evidence which suggests an essential dependence of numerical values of both f and k_d on the solvent[26–29]. A recent paper[41] indicates a solvation effect in the thermal decomposition of AIBN in monomer–solvent mixtures. Values obtained in our experimental conditions increase with the viscosities of the reaction mixtures and with the solvent polarity.

The temperature dependence for the effective rate coefficient, $2fk_d$, was found to be

$$2fk_d(s^{-1}) = 10^{15.83\pm0.92}exp((-131.7 \pm 5.6 \, kJ \, mol^{-1})/RT)$$

and

$$2fk_d(s^{-1}) = 10^{16.25\pm0.54}exp((-133.0 \pm 3.2 \, kJ \, mol^{-1})/RT)$$

for TO and BN, respectively.

Values ranging from 125 to 134 kJ mol^{-1} have been reported[28] for the activation energy of the decomposition rate constant for AIBN in various solvents.

Variations in $k_p/k_t^{1/2}$ in different solvents are well outside of experimental error and must be attributed to changes in one or both rate coefficients. Studies of the solvent effect on the radical polymerization show that k_p for MMA in TO is the same as in bulk[33] and k_p increases 5% relative to that in bulk when MMA is polymerized in BN[14,35]. We conclude that the variation of values of $k_p/k_t^{1/2}$ for MMA polymerization in the solvents used in this work are mainly due to changes in k_t.

In order to clarify the effect of solvents on the termination step, we must consider that the rate constant for the termination reaction decreases with increasing size of solvent macromolecules and is inversely proportional to the medium viscosity[1,14,16,25,42]. Considering separately the polymerization in each solvent, it seems clear that the higher $k_p/k_t^{1/2}$ values obtained in BN are due to a lower termination rate constant in this solvent than in TO as a consequence of the higher viscosity of the solution and a larger size of solvated macromolecule (see *Table 2*).

It is now recognised that the termination rate constant is dependent on the polymer chain length, in such a way that k_t decreases with increasing chain length[4–6]. When BN is used, molecular weights of the polymer are higher than those obtained when MMA is polymerised in TO. This factor will also contribute to a decrease of k_t when BN is used as a solvent.

The temperature dependence of the combined parameters $k_p/k_t^{1/2}$ obtained by combining two separate Arrhenius-type equations, is given by

$$\frac{k_p}{k_t^{1/2}} = \left(\frac{A_p}{A_t^{1/2}}\right)exp(-(E_p - E_t/2))/RT$$

Table 2 Analytical data at 25°C, for the homopolymerization of methyl methacrylate in different solvents

Solvent	η_{mix} (cp)	μ (D)	$[\eta]$ (ml g^{-1})	$(\bar{r}_0^2)^{1/2} \times 10^6$ (mm)
Bulk	0.533	1.67		
Benzonitrile	0.9780	4.18	28.5	10.01
Toluene	0.5516	0.375	25.0	9.58

η_{mix} = solution viscosity.
$[\eta]$ = intrinsic viscosity.
μ = dielectric constant.
$(\bar{r}_0^2)^{1/2}$ = root-mean-square end-to-end separation.

and from experimental results shown in *Table 1* we obtain

$$k_p/k_t^{1/2}(\text{mol}^{-1/2}\ \text{L}^{1/2}\ \text{s}^{-1/2}) = 10^{1.10\pm0.38}$$

$$\exp(-13.7 \pm 2.3\ \text{kJ mol}^{-1})/RT)$$

$$k_p/k_t^{1/2}(\text{mol}^{-1/2}\ \text{L}^{1/2}\ \text{s}^{-1/2}) = 10^{0.24\pm0.10}$$

$$\exp(-7.8 \pm 0.6\ \text{kJ mol}^{-1})/RT)$$

for TO and BN respectively.

Values between 11.2 and 15.4 kJ mol^{-1} have being calculated for $E_p - E_t/2$ from two different sets of data reported in a study of methyl methacrylate bulk polymerization[43] and a value of 16.5 kJ mol^{-1} has been calculated from the variations of $k_p/k_t^{1/2}$ with temperature in the ethyl methacrylate free radical polymerization[44].

Taking into account the value of E_p for methyl methacrylate free radical polymerization recently reported at the IUPAC Working Party on Modeling of Kinetics and Processes of Polymerization[45,46] and those of the ethyl metacrylate reported by Hutchinson et al.[47] we obtain values for the activation energies of the methyl methacrylate termination rate ranging between 22 and 14 kJ mol^{-1} and a value of 12 kJ mol^{-1} for ethyl methacrylate termination.

Considering that the value of k_p obtained when MMA is polymerised in TO is not significantly different from those obtained from MMA bulk polymerization and that the 5% increased in k_p relative to that obtained in bulk, when BN is used as a solvent, is independent of polymerizatioin temperature, we can assume that the activation energy of the propagation reaction is not affected by the solvents. In this case, termination activation energies differ by about 12 kJ mol^{-1} from TO and BN (17.3 and 29.1 kJ mol^{-1} for TO and BN, respectively). At first sight, this is difficult to explain, considering that radical–radical recombination is known to have a very low activation energy. However, the high value of E_t when MMA is polymerised in BN could arise from the temperature-dependent viscosity of the polymerization system and the chain length dependent k_t. The viscosity is lower at higher temperature, and the propagating polymer radical formed at higher temperatures has a shorter chain length. These factors could cause larger than expected k_t values at higher temperature, leading to higher apparent E_t values[48]. In this way, value of $E_t = 66.1$ kJ mol^{-1} has been reported for the free radical homopolymerization of disopropyl itaconate[48].

However, one precaution should be noted: it cannot be said with absolute certainty that E_p is independent of the solvent, since the variation of k_p measured in BN relative to that obtained in bulk may be dependent on polymerization temperature. Monterio and O'Driscoll have recently reported[49] that the propagation rate constant of MMA is a strong function of the monomer concentration when benzyl alcohol is used as a solvent. This fact has been attributed to the formation of radical chain end-solvent complexes. Experimental conditions, including variation of temperature should also be taken into account.

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