n-Dodecyl mercaptan transfer constant in polymerization of methyl methacrylate

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(Received 15 February 1993)

This paper investigates the effect of n-dodecyl mercaptan (n-DDM) as a chain transfer agent on the molecular weight of poly(methyl methacrylate). The transfer constant of n-DDM was calculated at different temperatures; the activation energy and frequency factor for an Arrhenius equation of transfer constant were then obtained.

(Keywords: poly(methyl methacrylate); chain transfer; molecular weight)

Introduction

The polymerization of methyl methacrylate (MMA) is accompanied by a very strong gel effect, which causes large increases in both reaction rate and the molecular weight of polymer produced. However, the molecular weight must be controlled to obtain a polymer with the desired mechanical properties for processing. Chain transfer agents are widely used for this purpose.

Chain transfer reaction is an atom abstraction process that may involve any species present in the polymerization medium, including monomer, initiator, chain transfer agent, etc. This process forms an inactive polymer molecule and a new radical which can reinitiate. Thiols, halogenated hydrocarbons and phenols are the most common chain transfer agents used in free-radical polymerization. Patent literature shows that mercaptans, especially n-dodecyl mercaptan, are widely used as chain transfer agents in MMA polymerization[1–3]. However, there are surprisingly few reports in the literature on MMA polymerization with mercaptans as chain transfer agents.

Walling[4] investigated MMA polymerization in the presence of thiols, using butylmercaptan and pentanemercaptan as chain transfer agents. The transfer constants were reported to be 0.80 for pentanemercaptan in the temperature range 40–100°C and 0.70 for butylmercaptan at 60°C. O'Brien and Gornick[5] examined two groups of mercaptans, aromatics and aliphatics. Chain transfer constants for two aromatic and five aliphatic thiols were determined; these were benzenethiol (2.7), 2-naphthalenethiol (3.0), 1-butanethiol (0.67), ethylmercaptoacetate (0.62), 2-mercaptoethanol (0.62), 2-propanethiol (0.38), and 2-methyl-2-propanethiol (0.18). The greater transfer activity of the aromatic thiols was attributed to a resonance stabilization of the corresponding sulfenyl radicals.

Barton *et al.*[6] investigated the effect of seven phenols and 10 aromatic thiols on the polymerization of MMA. They found that the aromatic thiols had transfer constants in the range 2.6–7.4 and concluded that they caused only slight retardation of polymerization. Dvornic and Jacovic[7] investigated the suspension polymerization of MMA in the presence of variable amounts of n-DDM at 70°C. This investigation focused on determining the viscosity of the reaction mixture at the onset of the gel effect. No experimental data regarding n-DDM transfer constant were reported. Abuin *et al.*[8] studied the effect of bromoform as a chain transfer agent on MMA polymerization at high conversion. Madruga *et al.*[9,10] studied the effect of n-DDM as a chain transfer agent on the onset and magnitude of autoacceleration as well as on limiting conversion in MMA solution polymerization. Giannetti *et al.*[11] carried out suspension polymerization of MMA in the presence of butyl and n-dodecyl mercaptan.

In all of these publications, no transfer constant value was reported for n-DDM. In this investigation, the transfer constant of n-DDM in MMA polymerization at various temperatures is calculated. The activation energy and frequency factor for an Arrhenius equation of transfer constant are also determined.

Experimental

MMA was purified prior to use. It was treated with 5% NaOH solution twice, then washed with distilled water three times and dried over sodium sulfate. It was then distilled under reduced pressure. Azobis(isobutyronitrile) (AIBN) from Merck was recrystallized three times from ethanol. n-DDM was used as received from Aldrich.

Homopolymerization reactions were conducted in Pyrex glass ampoules sealed under vacuum of 10^{-1} mmHg. The ampoules had a surface/volume ratio of 0.70 mm^{-1}, i.d. of 6.72 mm and thickness of 0.62 mm.

The polymerization reactions were conducted at four temperatures, 60, 70, 80 and 90°C. In all reactions the temperature was maintained constant within ± 0.1°C of the desired temperature. All runs were carried out by employing 0.3 wt% (with respect to weight of monomer) AIBN as initiator. n-DDM was used in several ratios in the range of 0.05–1.50 wt% (with respect to weight of monomer).

In the early stages of polymerization, the reaction was quenched by placing the ampoules in liquid nitrogen. The reaction mixture was dissolved in acetone containing

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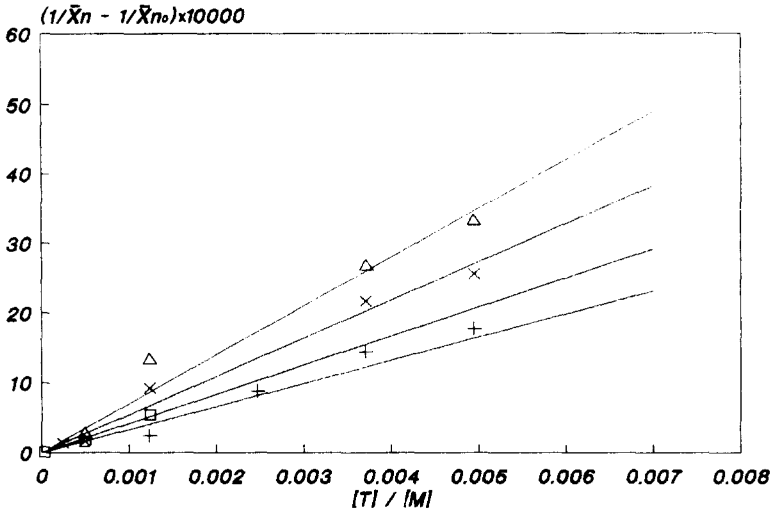

Figure 1 Mayo plot for n-DDM in MMA polymerization at: △, 60°C; ×, 70°C; □, 80°C; +, 90°C

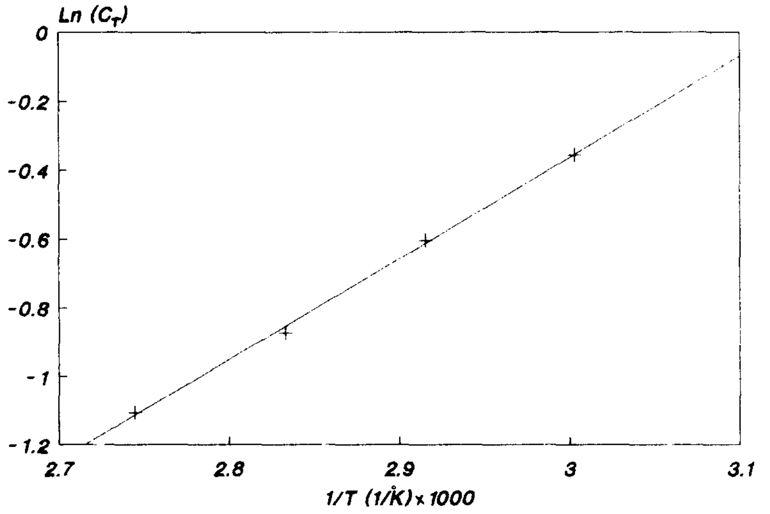

Figure 2 Arrhenius plot of C_T for n-DDM in MMA polymerization

Table 1 Transfer constants of n-DDM in MMA polymerization

Temperature (°C)	C_T
60	0.70
70	0.55
80	0.42
90	0.33

a very small amount of hydroquinone to prevent further polymerization. The polymer was precipitated out in a 20-fold excess of chilled methanol. The precipitated polymer was filtered and washed several times with fresh methanol. It was then dried at 50°C under vacuum for at least 48 h.

Molecular weights were measured at 30°C with a gel permeation chromatograph (Waters Associates, model 150-C). Four Styragel packed columns with different pore sizes (10^3–10^6 Å) were used. The mobile phase was tetrahydrofuran with a flow rate of 1.5 ml min^{-1}. The solution concentration was 0.2 wt%. Calibration of the instrument was performed with nine standard samples of monodisperse polystyrene with molecular weights between 3.0×10^3 and 1.4×10^6.

Results and discussion

Two methods are used to determine the transfer constant of a chain transfer agent. In the first method, the rate of disappearance of monomer and chain transfer agent are measured, then the transfer constant C_T is calculated from:

$$C_T = \frac{\mathrm{d}\log[\mathrm{T}]}{\mathrm{d}\log[\mathrm{M}]} \tag{1}$$

where [T] and [M] are the concentration of chain transfer agent and monomer, respectively. This method can be used when: (1) molecular weights are controlled by transfer to chain transfer agent; (2) the rate constants are not chain length dependent, even at low conversion.

In the second method, which is widely used, the chain transfer constant is determined from the slope of a Mayo plot:

$$\frac{1}{\bar{X}_n} = \frac{1}{\bar{X}_{n0}} + C_T \frac{[\mathrm{T}]}{[\mathrm{M}]} \tag{2}$$

where $\bar{X}_{n0}$ is the number-average degree of polymerization in the absence of chain transfer agent and $\bar{X}_n$ is that at a given [T]. This method can be used when: (1) the initiation rate is not modified by chain transfer; (2) the radicals produced in chain transfer reactions do not participate in termination and primary recombination reactions; (3) the rate constants are not chain length dependent. However, the modified Mayo equation can be applied when conditions (1) and (2) are not fulfilled[12]. In this investigation the second method (Mayo plot) is used.

Figure 1 plots the decrease in average chain length of polymer produced $(1/\bar{X}_n - 1/\bar{X}_{n0})$ *versus* [T]/[M], when chain transfer agent is used. The transfer constants were calculated from the slope of the best lines fitted to the experimental data, according to equation (2). *Table 1* lists calculated transfer constants of n-DDM at different temperatures. It is obvious from the results that the transfer constant decreases as the temperature increases. *Figure 2* plots $\ln(C_T)$ *versus* inversed temperature $(1/T)$. An Arrhenius equation was considered for C_T. Activation energy (E) and frequency factor (A) were calculated as presented in equation (3):

$$C_T = A_{tr}/A_p \exp[-(E_{tr} - E_p)/RT]$$

$$C_T = 7.5 \times 10^{-5} \exp[25289(\mathrm{J\,mol^{-1}})/RT(\mathrm{K})] \qquad (3)$$

The subscripts tr and p refer to chain transfer and propagation reactions, respectively.

This equation may be used for modelling and optimization of MMA polymerization in the presence of n-DDM as chain transfer agent. Further research on these topics is in progress.

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