Polymerization of methyl α-cyanoacrylate: 3. Study of radical polymerization by differential scanning calorimetry

John C. Bevington, John A. L. Jemmett* and (the late) Peter F. Onyon
Department of Chemistry, The University, Lancaster, UK
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A calorimetric method has been used to follow the free radical polymerization of methyl α-cyanoacrylate in bulk at 50°, 60° and 70°C and with nitromethane, benzene and dioxane as diluents at 60°C. In the initial stages, kinetic orders with respect to initiator were close to 0.5 even in systems where polymer separated as it was formed. For bulk monomer, polymerization ceased at about 90% conversion but resumed on raising the temperature. The heat of polymerization was ~42 kJ/mol.

INTRODUCTION

Isothermal differential scanning calorimetry (d.s.c.) can be used for kinetic studies of free radical polymerizations[1–3]. The technique has several distinct advantages in that it is quite simple, only small quantities of materials are required, results can be obtained quickly and reactions can be monitored continuously through to high conversions.

Conditions have been established[4] for dilatometric study of the early stages of the radical polymerization of methyl α-cyanoacrylate (MCA) without significant interference from anionic polymerization which occurs very readily for this monomer. Dilatometry is however of limited use because of the insolubility of the polymer in the monomer and in many other liquids. It appeared that d.s.c. might be useful for study of the polymerization of this monomer especially under heterogeneous conditions and in its later stages. It is essential to have a suitable inhibitor[1,3]; diphenylpicrylhydrazyl (DPPH) is satisfactory for use with MCA since it inhibits the polymerization almost completely and in so doing gives products which are only weak retarders[4].

This paper reports a calorimetric study of the radical polymerization of MCA at 50°, 60° and 70°C with bulk monomer and at 60°C with solutions in various liquids. Comparisons are made with the results of similar studies involving some other monomers in bulk.

EXPERIMENTAL

The purification of monomeric MCA has been described[5]; the final samples contained propane sultone† at 2.6×10^{-2} mol/dm^3 to suppress anionic polymerization. A Perkin–Elmer instrument (type DSC-1B) was used for calorimetry. Samples of about 20 mg were introduced into standard aluminium sample pans which were sealed in a press, washed with nitromethane acidified with phosphoric acid and then with acetone, and finally blown dry to constant weight. Any experiment accompanied by a weight loss exceeding 2% was rejected. DPPH was used at a concentration of $\sim 10^{-3}$ mol/dm^3. Reaction mixtures were made in ways designed to avoid casual variations between samples in a set of experiments. The procedures are illustrated by considering the study of the effect of concentration of initiator upon the bulk polymerization of MCA. A standard solution of DPPH in monomer containing propane sultone was divided into two portions; in one portion, initiator was dissolved to give the highest of the desired concentrations; all reaction mixtures were then made by mixing appropriate quantities of the two portions of monomer.

The use of the calorimeter has been described[1,3]. Fusion of benzoic acid was used for calibration. It was estimated that heats of polymerization were found with an error of ±2 kJ/mol.

RESULTS

Preliminary bulk polymerizations of MCA at 60°C, with azoisobutyronitrile (AIBN) or benzoyl peroxide (BPO) at fixed concentration, showed that the inhibition period was approximately proportional to the concentration of DPPH. Subsequently the rate of polymerization rapidly attained a value which increased slightly as reaction proceeded until auto-acceleration became pronounced (see *Figure 1a*). Systems were characterized by the rates when the inhibition was clearly over but auto-acceleration had not begun, as indicated by the intersection of broken lines in *Figure 1a*. Using rates so defined, the order with respect to initiator (AIBN or BPO) was close to 0.5, as found by dilatometry[4] and as expected for a normal radical polymerization.

Figure 1b shows exotherms for polymerizations of bulk MCA at 50°, 60° and 70°C. Although the reactions appeared to go to completion, further heat was evolved on raising the temperatures; a similar effect for methyl methacrylate[1] was shown to be due to incomplete consumption of monomer at the lower temperature. *Figure 2* shows that, when a sample pan was heated from 30° to 160°C in the calorimeter, polymerization was resumed when the temperature of the pan exceeded that at which the original isothermal polymerization had been performed. Evidently reaction was complete in this second stage because there was no evolu-

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* Present address: General Foods Limited, Banbury, Oxfordshire, UK.

† Warning – this substance is now known to be carcinogenic.

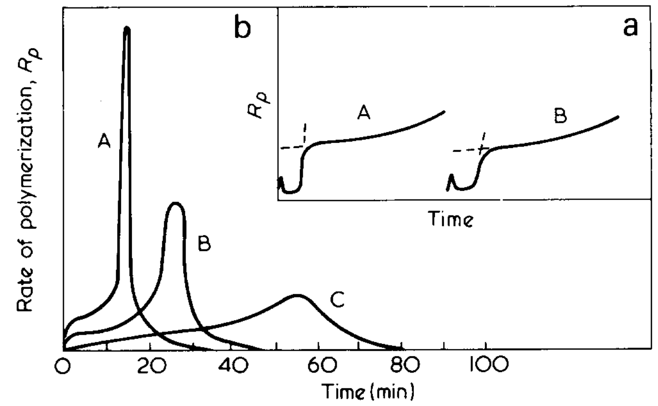

Figure 1 (a) Exotherms for polymerizations of bulk MCA at 60°C with AIBN at 6.38 × 10^{-2} mol/dm^3. Initial concentrations of DPPH: A, 3.41 × 10^{-4} mol/dm^3 (induction period ~50 sec); B, 6.84 × 10^{-4} mol/dm^3 (induction period ~100 sec). (b) Exotherms for polymerizations of bulk MCA with AIBN at 6.6 × 10^{-2} mol/dm^3 and DPPH at 1.3 × 10^{-3} mol/dm^3. A, 70°C; B, 60°C; C, 50°C

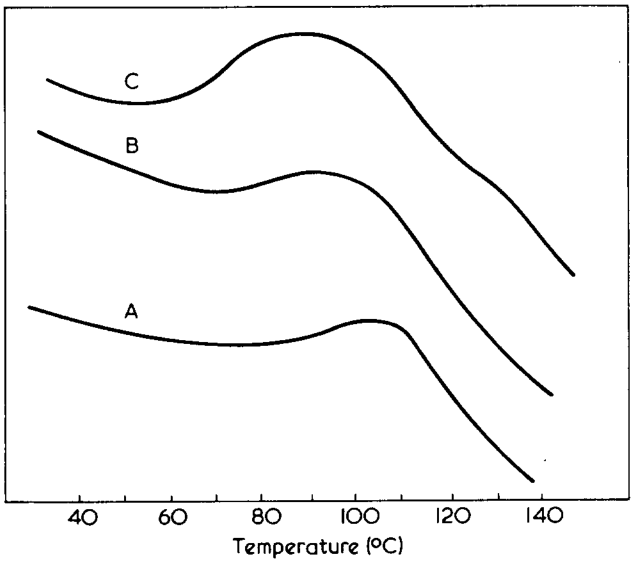

Figure 2 D.s.c. scans for MCA samples referred to in *Figure 1b*; scanning rate, 4°C/min

tion of heat during a further scan from 30° to 160°C. From the primary and secondary exotherms and the calibration with benzoic acid, values of the heat of polymerization were found to be 45, 42 and 40 kJ/mol respectively for reactions performed at 50°, 60° and 70°C; the corresponding limiting conversions were 88, 92 and 94%.

The calorimetric method was used for study of the radical polymerization of MCA in solution. Nitromethane is a solvent for the polymer and, as expected, its presence during polymerization at 60°C caused auto-acceleration to be less pronounced than for bulk monomer; the order with respect to monomer was about 2.2 in the early stages of reaction. Other liquids known to dissolve polyMCA were completely unsatisfactory as diluents; they gave rise to severe irreproducibility and rapid polymerizations even in the absence of radical sources such as AIBN and BPO.

The dilatometric method can be applied to the initial stages of polymerization of MCA in dioxane at 60°C although polymer separates as a gel[4]; the previous results were confirmed by the calorimetric method. The polymer is insoluble in benzene also but dilatometry cannot be used for study of the polymerization; the calorimetric method however gave quite reproducible results. Auto-acceleration was pronounced but, from the initial rates, the order with respect to monomer was about 1.2.

Exotherms for bulk polymerizations of methyl acrylate and acrylonitrile at 60°C are shown in *Figure 3*. For the methyl acrylate sample, subequent heating from 30° to 160°C gave no exotherm and it appears that reaction was complete in the first stage; the heat of polymerization was found to be 75 kJ/mol. For acrylonitrile, further heating of the sample showed that 6% of the monomer did not polymerize at 60°C; from the primary and secondary exotherms, it was deduced that the heat of polymerization is 75 kJ/mol. The conversion/time plots in *Figure 4* were derived from exotherms shown in *Figures 1b* and *3*, the weights of monomers involved and the heats of polymerization.

DISCUSSION

Results such as those in *Figure 1a* indicate that DPPH is satisfactory as an inhibitor for use with MCA in kinetic studies by d.s.c. After the inhibition period, auto-acceleration becomes pronounced only after an interval during which the rate is fairly steady at a value almost independent of the initial concentration of inhibitor. The heats of polymerization (75 kJ/mol) found for acrylonitrile and methyl acrylate are not of great precision and do not refer to standard conditions but they are in fair agreement with literature values[6] (~75.2 kJ/mol for acrylonitrile and 78.6 kJ/mol for methyl acrylate). The value of 42 kJ/mol for MCA can therefore be accepted as reasonable. The low heat of polymerization can be attributed in part to destabilization of the polymer caused by the presence of two quite large substituents on alternate carbon atoms along the main chain, and in part to stabilization of the monomer due to conjugation of its C=C bond with the nitrile and ester groups.

For polymerizations at 60°C, the limiting conversions for bulk MCA and acrylonitrile were 92 and 94% respectively but methyl acrylate reacted completely. Of the three monomers, only methyl acrylate gives a polymer with a glass transition temperature below 60°C. Horie *et al.*[1] attributed the failure to achieve complete polymerization during similar experiments with methyl methacrylate to the fact that the reaction temperature was below

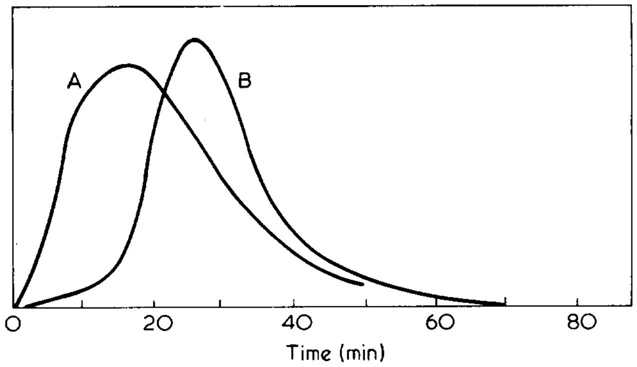

Figure 3 Exotherms for polymerizations of bulk monomers at 60°C. A, Acrylonitrile with AIBN at 9.96 × 10^{-2} mol/dm^3; B, methyl acrylate with AIBN at 7.24 × 10^{-2} mol/dm^3; in both cases, DPPH at ~1.5 × 10^{-3} mol/dm^3

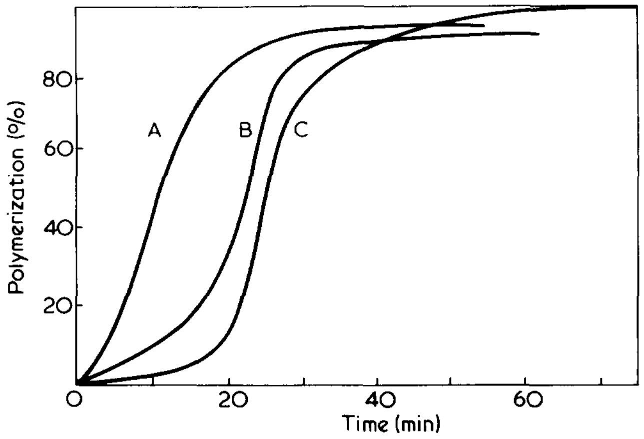

Figure 4 Conversion/time plots for bulk monomers at 60°C: A, acrylonitrile; B, MCA; C, methyl acrylate. Conditions as specified for *Figures 1b* and *3*

T_g for the system so that mobilities of radicals and residual monomer were very restricted in systems consisting almost entirely of polymer. This explanation seems to be valid also for MCA and acrylonitrile.

Figure 4 confirms that auto-acceleration for methyl acrylate begins very early in the polymerization; in this system, except perhaps at quite high conversions when crosslinking may be possible, the polymer is soluble in the monomer and termination is diffusion controlled. The exotherm for bulk acrylonitrile has a different form; for this monomer, acceleration is attributed[7] to the trapping of radicals in precipitated polymer so that termination is impeded although the growth reaction is comparatively little affected. For polymerization of bulk MCA at 70°C, the system remains homogeneous and the auto-acceleration is associated with diffusion control of termination as in the case of methyl acrylate. At 60°C, solubility of the polymer in the monomer is limited and gel separates but the kinetic effects are different from those for acrylonitrile in that there is a period when the rate of polymerization is almost steady and the order with respect to initiator is close to 0.5. The exotherms for polymerizations of bulk MCA at 60° and 70°C (*Figure 1b*) are very similar in shape and it appears that polymer radicals in the gel at 60°C must have appreciable mobility. The exotherm for reaction at 50°C is rather different probably because the polymer possesses hardly any solubility in the monomer at this lower temperature.

The homogeneous radical polymerization of MCA in nitromethane could not be studied by dilatometry because solutions of the monomer in this liquid quite quickly became sensitive to anionic polymerization in spite of the presence of propane sultone; the system could however be studied by the calorimetric method which permitted more rapid working. Auto-acceleration was pronounced in the later stages; the order of 2.2 with respect to monomer, found from rates in the early stages, must be due to retardation caused by the solvent.

Polymerizations of MCA in dioxane and benzene at 60°C were heterogeneous. The calorimetric method showed that, with both diluents, there were limited periods of almost steady polymerization before auto-acceleration set in; the orders with respect to initiator and monomer were nearly 0.5 and a little over 1.0 respectively. Polymerizations in these diluents resemble the bulk polymerization at 60°C and, in spite of heterogeneity, the kinetic characteristics in the early stages are not appreciably different from those expected for a 'normal' radical polymerization.

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