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Synthesis of arsenic containing polymethylmethacrylate using *p*-acetyl benzylidene triphenyl arsonium ylide as photoinitiator

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Abstract

Arsenic containing syndiotactic polymethylmethacrylate (PMMA) using p-ABTAY (p-acetyl benzylidene triphenyl arsonium ylide)in benzene as the photoinitiator at 30 ± 0.2°C has been synthesized. The system follows non-ideal kinetics ($R_p \propto [I]^{0.25}$ [M]) due to both primary radical termination and degradative chain transfer reaction. The glass transition temperature of PMMA is 145°C. Analysis of the polymer by SEM technique shows the presence of arsenic in it. The polymer has been characterized by Infra-red spectroscopy.

Keywords: Arsenic; Polymethylmethacrylate; Photoinitiator

1. Introduction

Photopolymerization is concerned with the creation of a polymer through a chain reaction that has been initiated by light. In commercial practice, most compounds which absorb light and produce a chain initiating event, photoinitiating event, photoinitiators, operate below 400 nm [1]. Much effort has been devoted to free radical photoinitiated polymerization mainly due to the availability of a wide range of photoinitiators [2].

A search of literature reveals that few compounds such as *N*-alkoxy pyridinium [3] and *N*-isoquinolium salts [4] have been shown to act as photoinitiator for cationic and free radical polymerizations. However, little attention has been paid to the use of arsonium ylide [5]. This paper highlights the use of arsonium ylide as photoinitiator for the polymerization of MMA. As far as we know this is the first study regarding the formation of a metal containing insoluble PMMA.

2. Experimental

MMA and solvents were purified by standard method [6]. Triphenyl arsine (Merck-Art 808653) was used as received in the preparation of ylide.

2.1. Preparation of ylide

The ylide *p*-ABTAY was prepared by the method [7] which is briefly given below.

2.1.1. Synthesis of p-bromomethyl acetophenone

To an ice cold solution of *p*-methyl acetophenone, bromine was added dropwise and after complete addition, the mixture was stirred. Thereafter, the stirred mixture was decomposed by pouring it into an ice cold water. The white ppt. formed was the bromide of *p*-methyl acetophenone, which was separated by filtration.

2.1.2. Synthesis of p-acetyl benzylidene triphenyl arsonium bromide

An equimolar solution of triphenyl arsine and *p*-bromo methyl acetophenone in benzene was refluxed for 72 h. Excess of solvent was evaporated and ethyl acetate was added to the residue. The precipitated salt was isolated by filtration and recrystallized from chloroform–benzene mixture (v/v).

2.1.3. Generation of p-acetyl benzylidene triphenyl arsonium ylide

p-Acetyl benzylidene triphenyl arsonium bromide in benzene was treated with sodium ethoxide in methanol, whereby a yellow suspension of ylide was obtained.

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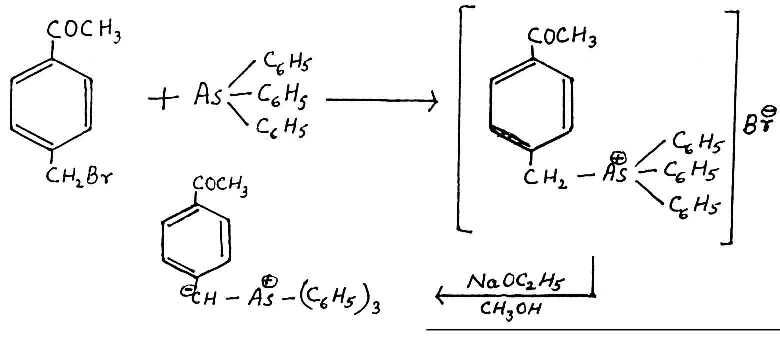


2.2. Polymerization technique

Methyl methacrylate was purified and charged to a quartz ampoule with solvent (benzene) and the photoinitiator (*p*-ABTAY). This was covered with a blanket of nitrogen and irradiated using a Philips (125 W) high pressure mercury lamp (path length 10 cm, 440 nm interference filter). Polymers formed at low conversions were precipitated with excess of acidified methanol and then dried to a constant weight. The rate of polymerization (R_p) was calculated from the slope of the percentage conversion vs. time plots. The polymer was characterized using IR, DSC and SEM technique. NMR spectroscopy could not be carried out due to the insolubility of the polymer in most of the organic solvents.

2.3. Infra-red spectrum

The infra-red spectrum was recorded on a Perkin-Elmer Spectrophotometer (Model 377) using KBr pellets.

2.4. Scanning electron microscopy (SEM)

Scanning electron micrographs were obtained from a Jeol JSM 840 A scanning electron microscope. The film was mounted vertically on a SEM stub using silver adhesive paste.

2.5. Differential scanning calorimetry (DSC)

DSC was carried out on V4.1C Dupont 2000 at the heating rate of 10°C min^{-1}.

3. Results and discussions

No polymer was obtained when MMA alone was exposed to light or when MMA and *p*-ABTAY were left in the dark. The results of MMA polymerization which proceeds with an induction period of about 18 h are illustrated in Figs. 1–3.

The effect of *p*-ABTAY on the rate of polymerization (R_p) was studied by varying the concentration of *p*-ABTAY from 2.28×10^{-4} to 22.8×10^{-4} mol l^{-1} at a fixed intensity of light. R_p increases with increasing concentration of ylide (Table 1). The initiator exponent, calculated from the slope of the plot of log R_p vs. log [*p*-ABTAY] is 0.25 (Fig. 4). This value is less than as expected for ideal radical kinetics.

Values of R_p also increases with the increasing concentration of MMA from 0.89×10^{-5} to 4.27×10^{-5} mol l^{-1} (Table 2) and the monomer exponent, calculated from the

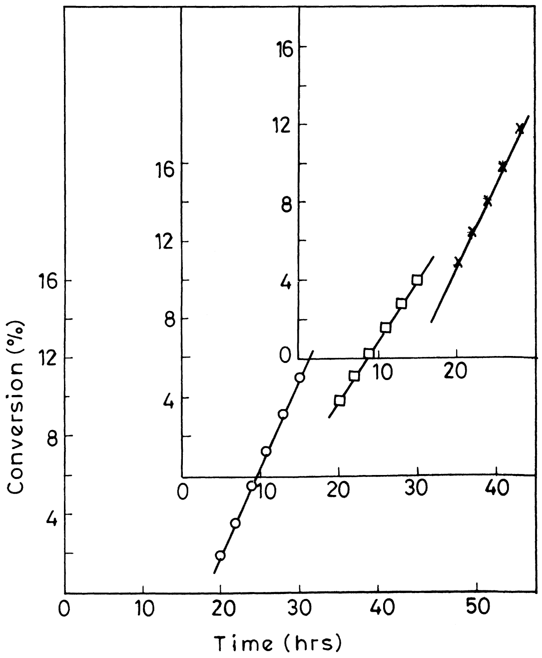


Fig. 1. Time conversion plot for the polymerization of MMA. [MMA] = 3.56×10^{-5} mol l^{-1}. Time = 30 h. Temperature = 30 ± 0.2°C. [*p*-ABTAY]: 0 = 2.28×10^{-4} mol l^{-1}; □ = 4.56×10^{-4} mol l^{-1}; x = 9.13×10^{-4} mol l^{-1}.

Table 1
Effect of [ylide] on polymerization

S. No.	*p*-ABTAY $\times 10^4$ mol l^{-1}	Percent conversion	$R_p \times 10^7$ mol l^{-1} s^{-1}
1	2.28	9.5	4.70
2	4.56	10.0	4.86
3	9.13	12.5	6.26
4	13.6	12.2	6.16
5	18.2	12.7	6.96
6	22.8	12.8	6.80

[MMA] = 3.56×10^{-5} mol l^{-1}.
Temperature = 30 ± 0.2°C.
Time = 30 h.

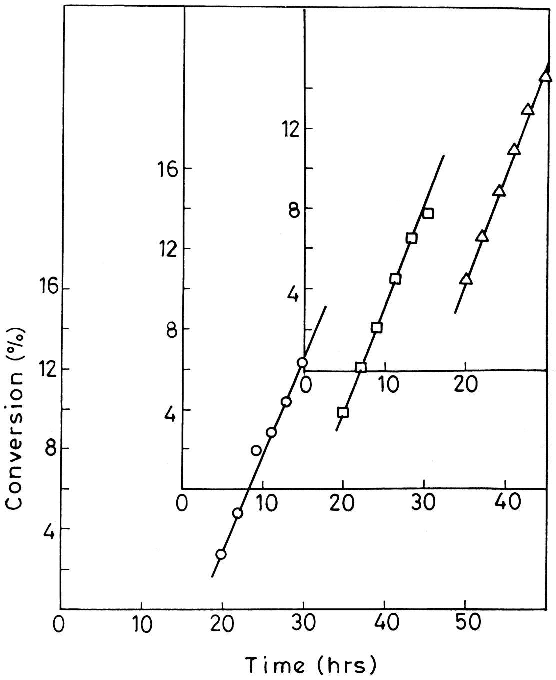


Fig. 2. Time conversion plot for the polymerization of MMA. [MMA] = 3.56×10^{-5} mol l^{-1}. Time = 30 h. Temperature = 30 ± 0.2°C. [p-ABTAY]: 0 = 13.5×10^{-4} mol l^{-1}; □ = 18.2×10^{-4} mol l^{-1}; Δ = 22.8×10^{-4} mol l^{-1}.

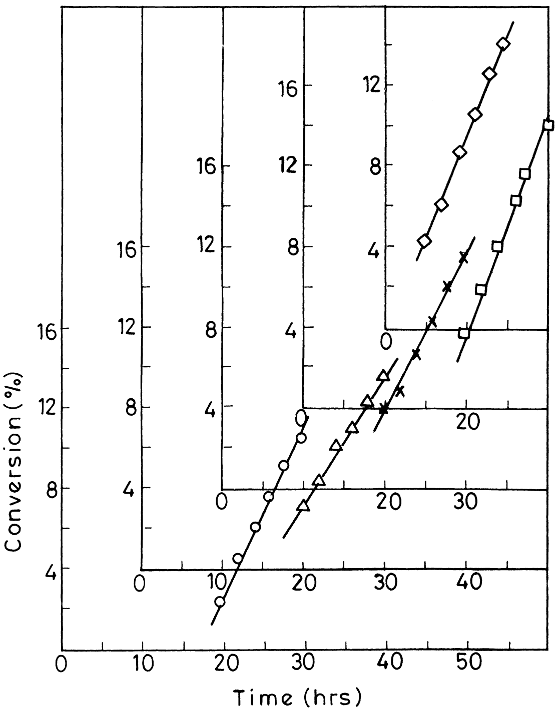


Fig. 3. Time conversion plot for the polymerization of MMA. [p-ABTAY] = 9.13×10^{-4} mol l^{-1}. Time = 30 h. Temperature = 30 ± 0.2°C. [MMA] 0 = 0.89×10^{-5} mol l^{-1}; Δ = 1.78×10^{-5} mol l^{-1}; x = 2.67×10^{-5} mol l^{-1}; □ = 3.50×10^{-5} mol l^{-1}; ◇ = 4.27×10^{-5} mol l^{-1}.

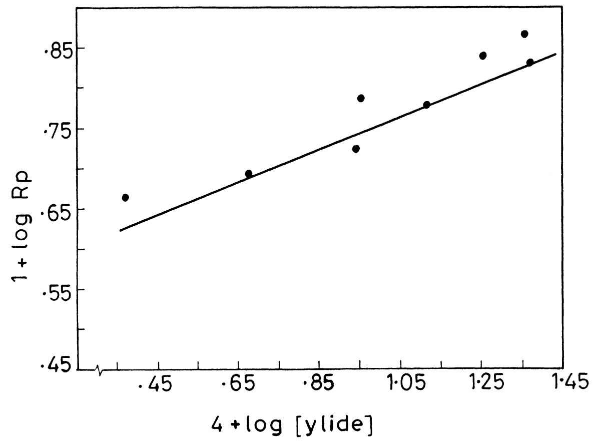


Fig. 4. Plot of log R_p vs. log [ylide]. [MMA] = 3.56×10^{-5} mol l^{-1}. Time = 30 h. Temperature = 30 ± 0.2°C.

slope of the linear plot of log R_p vs. log [MMA], is unity (Fig. 5).

The low value of initiator exponent suggests that the system follows non-ideal kinetics. The kinetic non-ideality can be explained by analyzing the role of p-ABTAY as primary radical terminator and degradative chain transfer agent.

To analyze the effect of primary radical termination a suitable modified expression given by Deb and Meyerhoff [8] in the following form is used:

$$\log \frac{R_p^2}{[Y][M]^2} = \log \frac{2f_kK_dK_p^2}{K_t} - 0.8684\frac{K_{prt}}{K_Y \times K_p} \times \frac{R_p}{[M]^2}$$

where Y and M represent ylide and monomer, respectively. A plot of the left hand side of the above equation vs. $R_p/[M]^2$ gave a negative slope (Fig. 6) indicating primary radical termination due to ylide for the present system.

The following equation derived by Deb [9] and further simplified by Ghosh and Mitra [10] was used to examine the role of ylide as degradative chain transfer agent:

$$\log \frac{R_p^2}{[Y][M]} = \log\frac{2f_kK_dK_p^2}{K_t} - 0.434\frac{K_P^2}{K_t} \times \frac{K_{rt}Y}{K_YYK_p} \times C_1\left[\frac{Y}{M}\right]$$

where C_1 is the ylide transfer constant. The plot of the left hand side of the above equation vs. [Y]/[M] also gave a

Table 2
Effect of [MMA] on polymerization

S. No.	MMA $\times 10^5$ mol l^{-1}	Percent conversion	$R_p \times 10^7$ mol $l^{-1}s^{-1}$
1	0.89	8.74	1.18
2	1.78	9.69	1.72
3	2.67	10.28	3.91
4	3.56	12.50	6.26
5	4.27	12.84	6.62

[p-ABTAY] = 9.13×10^{-4} mol l^{-1}.
Temperature = 30 ± 0.2°C.
Time = 30 h.

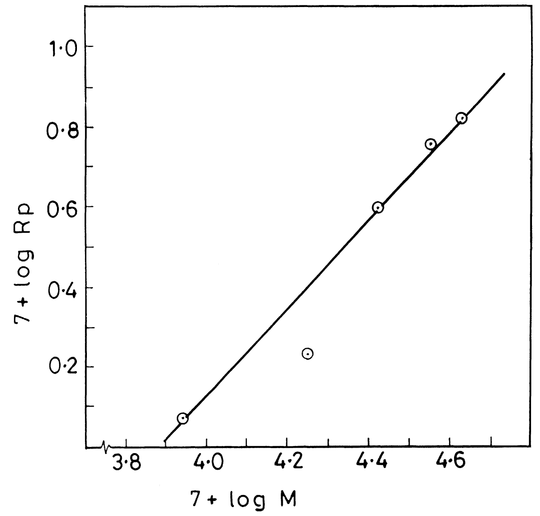


Fig. 5. Plot of $\log R_p$ vs. log [monomer]. [p-ABTAY] = 9.13 × 10^{-4} mol l^{-1}. Time = 30 h. Temperature = 30 ± 0.2°C.

negative slope (Fig. 7) suggesting degradative chain transfer reaction due to ylide.

Viscosity measurements and molecular weight calculations of the polymer could not be carried out due to its insolubility in most of the organic solvents.

The IR spectrum of PMMA (Fig. 8) consists of four groups of bands

1. The range of C–H stretching vibrations is dominated by the methyl and methylene groups, which shows bands at 3000 and 2960 cm^{-1}, respectively.
2. The C=O stretching range shows a strong homogenous ester carbonyl band at 1735 cm^{-1}.
3. C–H deformation range showing bands in the region 1365–1490 cm^{-1}.
4. The ester stretching band (C–O–C) appears in the region 1150–1275 cm^{-1}.

The band at 1060 cm^{-1} is only noticed in syndiotactic PMMA [11].

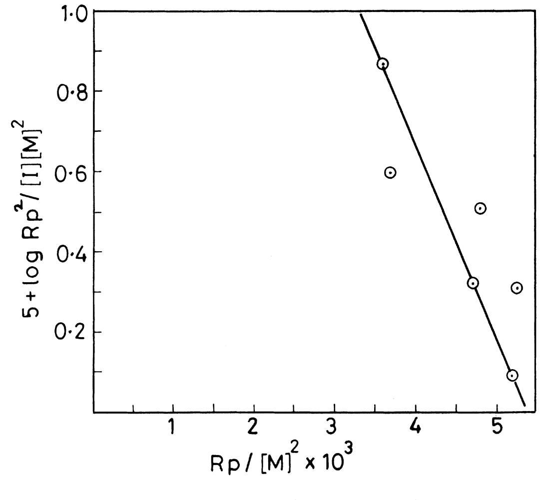


Fig. 6. Plot between $\log R_p^2/[I]\ [M]^2$ vs. $R_p/[M]^2$ [MMA] = 3.56 × 10^{-5} mol l^{-1}. Time = 30 h. Temperature = 30 ± 0.2°C.

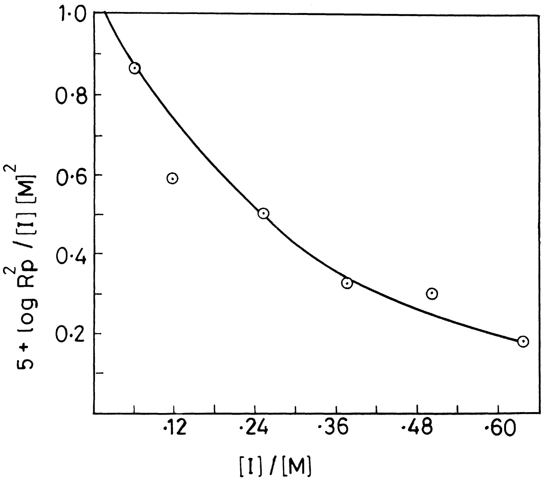


Fig. 7. Plot between $\log R_p^2/[I]\ [M]^2$ vs. [I]/[M] [MMA] = 3.56 × 10^{-5} mol l^{-1}. Time = 30 h. Temperature = 0.2°C.

Synodiotacticity is well confirmed by using NMR spectroscopy [12]. In our case NMR could not be used to confirm syndiotacticity because of the insolubility of polymer due to the incorporation of Arsenic in it.

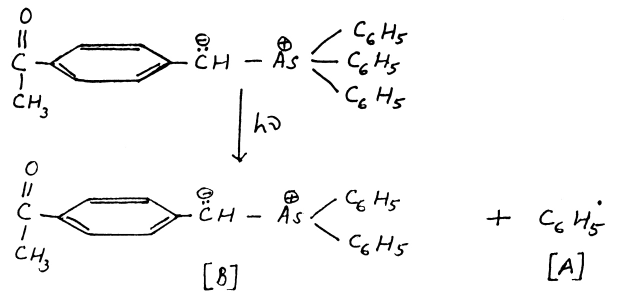
Differential scanning calorimetry (DSC) (Fig. 9) technique has been used to measure the glass transition temperature (T_g) of arsenic containing poly (MMA). It was found to be 145°C which is quite high as compared to the reported value of 105°C for syndiotactic PMMA. This may be attributed to the crosslinking as well as the presence of As in the polymer.

Scanning electron microscopy (SEM) pictures (Fig. 10) show two-phase morphology indicating the presence of Arsenic in the paper. The presence of Arsenic is also confirmed by the qualitative test [13] using conc. HNO_3 and ammonium molybdate, when yellow ppt. was obtained.

4. Mechanism

Earlier reports [5] suggest arsonium ylide undergoes bond fission between the heteroatom and the phenyl group and the phenyl radical produced participates in the initiation of photopolymerization.

This was confirmed by the gas–liquid chromatography (CIC Model 8.6- pro.gas chromatograph with casbowax 20 m column) of p-ABTAY solution in presence of toluene in the system. The formation of toluene indicates the existence of the phenyl radical.



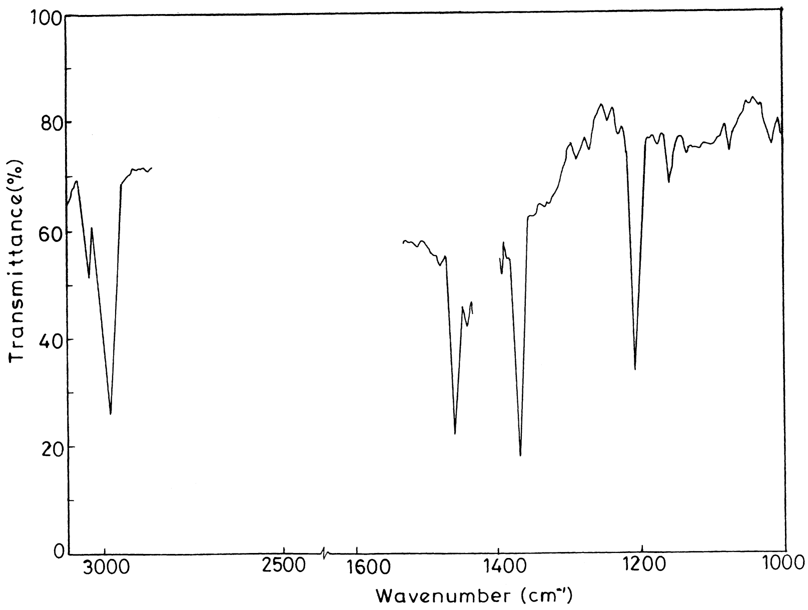


Fig. 8. IR spectra of PMMA.

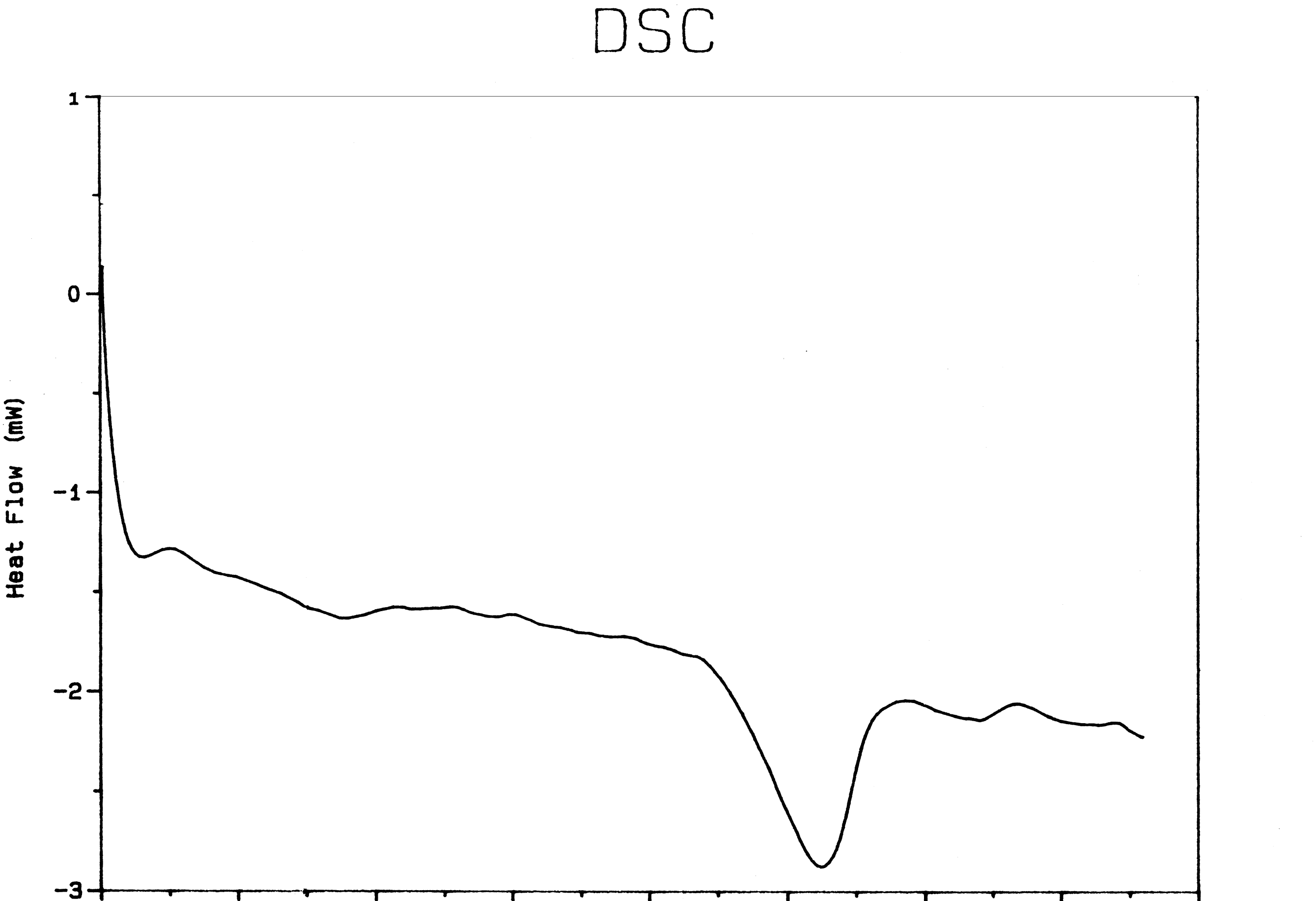


Fig. 9. DSC curve of PMMA.

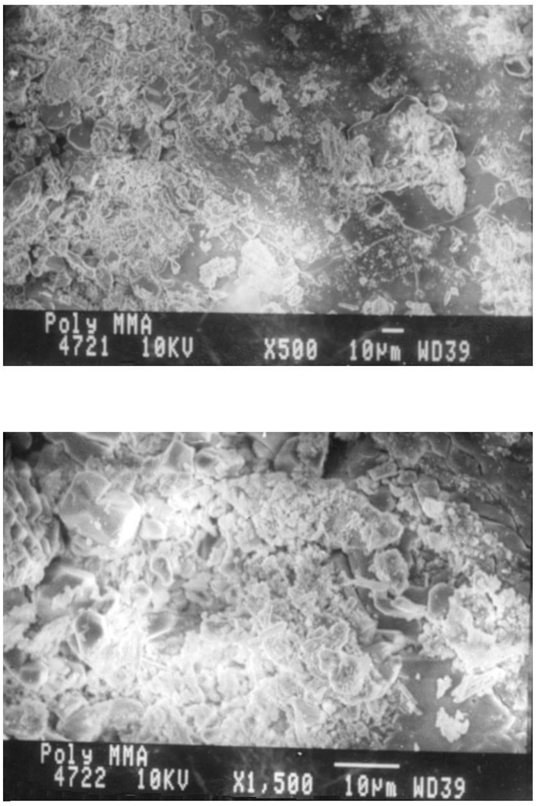


Fig. 10. SEM photograph of PMMA.

The presence of As in the polymer suggests that the radical [B] causes simultaneous initiation as well as some degree of crosslinking. Besides the long used periods of UV irradiation might have caused crosslinking. Both factors seem to be responsible for the insolubility of the polymer in most of the organic solvents.

Acknowledgements

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