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Preparation of diblock copolymer of methyl methacrylate and vinyl acetate by successive radical mechanism and selective hydrolysis of the poly(vinyl acetate) block

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The preparation of a block copolymer of methyl methacrylate (MMA) and vinyl acetate (VAc) (PMMA-*b*-PVAc) was carried out by successive charge-transfer polymerization (CTP) in aniline–benzophenone as binary initiation system under ultraviolet irradiation; subsequently a block copolymer of PMMA and poly(vinyl alcohol) (PMMA-*b*-PVA) was derived by selective hydrolysis of PMMA-*b*-PVAc in ethanolic sodium ethoxide. These copolymers were characterized in detail by means of Fourier transform infra-red and proton nuclear magnetic resonance spectroscopies, and gel permeation chromatography. The solvent polarity exerts an effect on the copolymerization. © 1997 Elsevier Science Ltd. All rights reserved.

(Keywords: charge-transfer polymerization; methyl methacrylate; vinyl acetate)

INTRODUCTION

Much attention has been focused on block copolymers of poly(methyl methacrylate) (PMMA) in the field of block copolymer compatibilizers for polymer blends[1–3] because PMMA is compatible with several important polymers such as poly(styrene-*co*-acrylonitrile), poly(vinyl chloride) and poly(vinylidene fluoride).

In relation to the spinodal decomposition of polymer blends, the effect of a block or graft copolymer as compatibilizer is of particular interest. Extensive investigations have been carried out on the effect of a series of diblock copolymers such as polystyrene-*b*-polybutadiene (PS-*b*-PB)[4,5] and polystyrene-*b*-polymethylphenylsiloxane (PS-*b*-PMPS)[6] on their blend pairs. These systems display an upper critical solution temperature (UCST) in which the blend pairs are immiscible and phase-separated at low temperature but miscible and homogeneous at higher temperature. However, the effect of block copolymers on some blend systems with a lower critical solution temperature (LCST)—which, in contrast to blends displaying USCT behaviour, are homogeneous and miscible at low temperature and immiscible at high temperature—has not yet been studied in detail owing to the difficulty of synthesizing the corresponding block copolymers. Examples of the latter type of system include PMMA/poly(vinyl acetate) (PVAc)[7] and PS/poly(methyl vinyl ether) (PVME)[8].

In the preparation of block copolymers, anionic living polymerization is generally the most useful procedure. However, it is only suitable for some monomers with low polarity such as styrene, butadiene, isoprene and others, and is inapplicable for monomers such as vinyl acetate, vinyl alkyl ketone and so on.

This paper is centred on the preparation of a block copolymer of methyl methacrylate (MMA) and vinyl acetate (VAc) by sequential radical polymerization using a photo-induced charge-transfer complex composed of aniline and benzophenone (BP) as initiator. The copolymer so formed was selectively hydrolysed to form PMMA-*b*-poly(vinyl alcohol) (PVA). Investigation of the morphology and compatibility of PMMA-*b*-PVAc with the corresponding homopolymer pair will be reported elsewhere.

EXPERIMENTAL

Materials

Aniline (Shanghai First Reagent Factory, China) was dried over 4 Å molecular sieves and then distilled under reduced pressure; the fraction of 65°/8 mm being collected. MMA, VAc and all solvents were purified by standard methods[9]. Benzophenone (BP) was recrystallized twice from ethanol.

Photochemical-induced CTP of MMA using aniline–BP pair

In a typical polymerization procedure (*Scheme 1*), aniline (0.0093 g, 1.0×10^{-4} mol), BP (0.0182 g, 1.0×10^{-4} mol, benzene (5 ml) and MMA were added to a 100 ml ampoule and the mixture degassed. After three cycles of freeze–pump–thaw at 77 K, the ampoule was sealed and irradiated with a 300 W high-pressure mercury lamp (model DDZ-300, manufactured by Shanghai Ya Ming Lamp Factory) for 24 h at 25°C under N_2. Cupric sulfate aqueous solution was used as photofilter to obtain 365 nm monochromic light[10]. The product was precipitated in methanol, and

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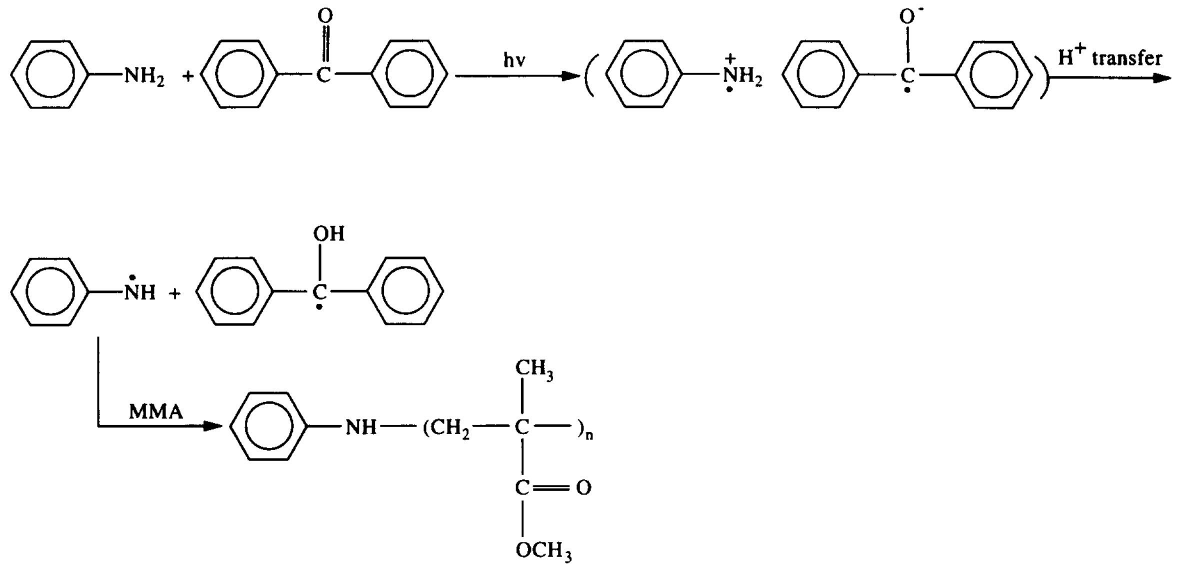
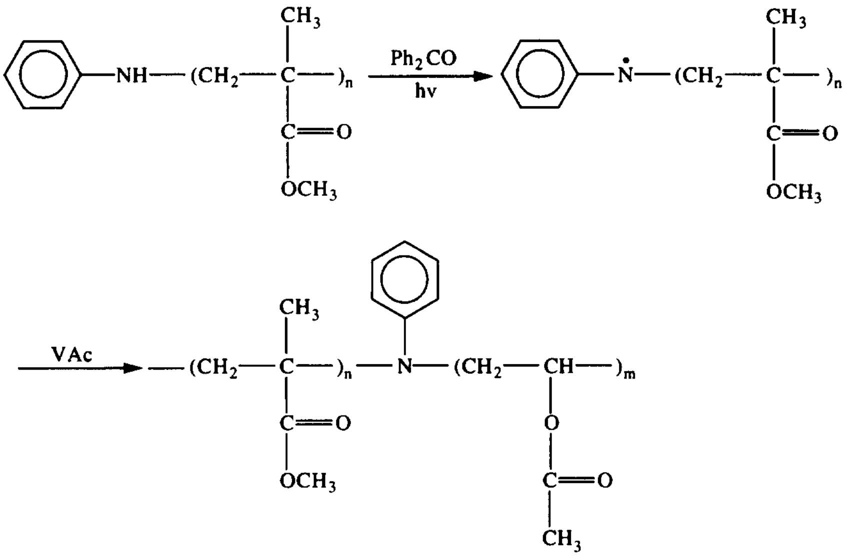


Scheme 1



Scheme 2

purified by dissolution/precipitation from chloroform into methanol in a yield of 83.26% (3.93 g). I.r. (cm^{-1}): 1732 (–CO); ^{1}H n.m.r. (δ, ppm): 0.85, 1.02, 1.22 (C–CH_3 for syndio-, hetero- and isotactic, respectively), 1.82 (–CH_2–) and 3.60 (–OCH_3).

Block copolymerization of VAc

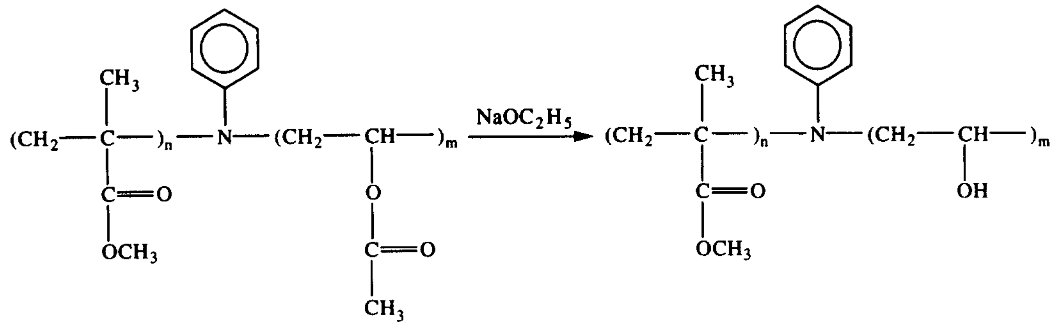
PMMA prepolymer with aromatic imino end groups (0.808 g, 8.0 × 10^{-5} mol) was dissolved in 5 ml benzene. The solution was introduced into a 100 ml ampoule to which BP (0.0146 g, 8.0 × 10^{-5} mol and VAc (5 ml) were added (*Scheme 2*). The degassing and polymerization procedure were the the same as for the preparation of PMMA prepolymer. The diblock copolymer was purified as follows: it was dissolved in chloroform and the solution was added slowly to methanol to remove unreacted PMMA homopolymer by precipitation (0.25 g), after filtration ether was added to the filtrate to precipitate the remaining polymer. The precipitated polymer was extracted with methanol in an attempt to isolate the PVAc homopolymer, but no trace of PVAc was found. The final product weighed 0.85 g.

*Hydrolysis of PMMA-**b**-PVAc*

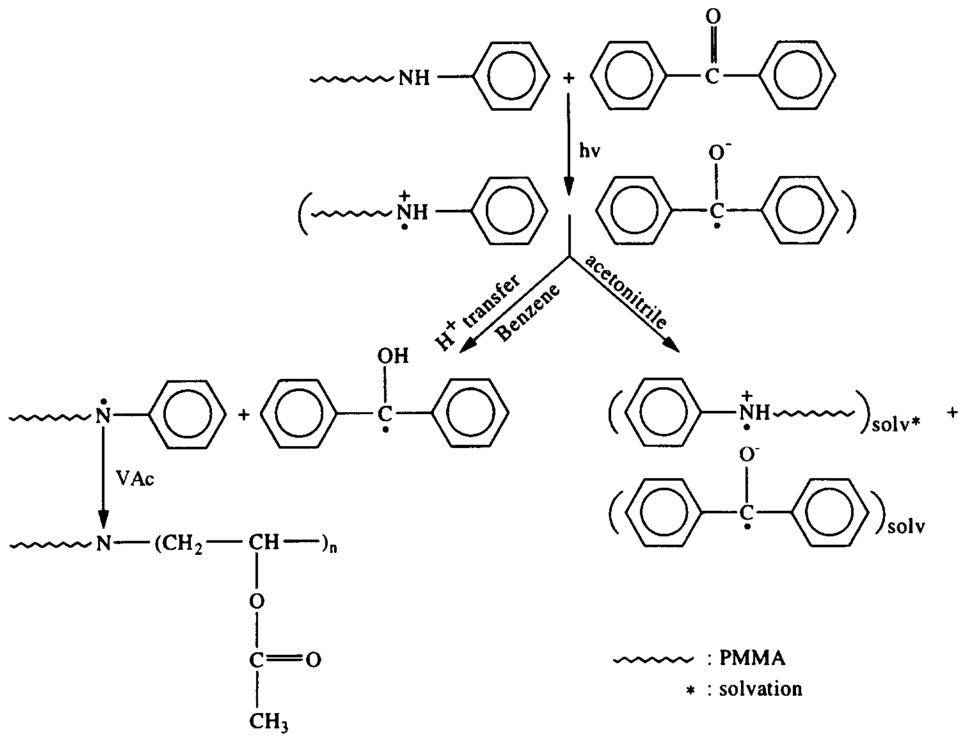
To a 100 ml three-necked flask fitted with a mechanical stirrer, funnel and thermometer, the diblock copolymer (1.00 g, 2.8 × 10^{-5} mol) and benzene (20 ml) were added. The block copolymer was dissolved at 70°C, and then 5% ethanolic sodium ethoxide (5 ml) was added dropwise from the funnel. After about 2 h with stirring at 70°C, the flask was cooled to room temperature. The product was precipitated in ether, then extracted with chloroform to remove the unhydrolysed copolymer (*Scheme 3*). The hydrolysis was carried out to completion; no original copolymer was detected by i.r. and n.m.r. The final weight of hydrolysed product was 0.73 g.

Kinetic measurements

The kinetics of charge-transfer polymerization (CTP) were investigated by using a modified dilatometer which



Scheme 3



Scheme 4

could be evacuated, so that the influence of oxygen on the polymerization was reduced. The capillary diameter and the volume of the dilatometer bulk were calibrated three times with water and mercury at 25°C. The measurement conditions were the same as those described in Section 2.2 for CTP, the incident light intensity on the surface of dilatometer being 0.5 kW m^{-2}. The kinetic runs took 40 min and readings were recorded at intervals of 5 min.

Instruments

Infra-red spectra were obtained on a Magna-550 Fourier transform infra-red (*FT*i.r.) spectrometer. ^{1}H nuclear magnetic resonance (n.m.r.) spectra were recorded on a Bruker MSL-300 spectrometer with tetramethylsilane (TMS) as the internal standard and deuterochloroform ($CDCl_3$) [or deuterated dimethyl sulfoxide (DMSO–d_6)] as the solvent. The molecular weight and molecular weight distribution were derived by means of gel permeation chromatography (g.p.c.) on a Shimadzu LC-3A chromatograph with a microcomputer using refractive index for detection [column length: 1.2 m; filler: crosslinked polystyrene gel (1250 mesh); injection volume: 1.0 ml; solvent and eluent: chloroform; flow rate: 1.0 ml min^{-1}; pump pressure: 40 kg cm^{-2} (3.99×10^6 Pa)]. The instrument was calibrated with standard polystyrene samples.

RESULTS AND DISCUSSION

Effect of solvent polarity on block copolymerization

As is well known, solvents do not exert a great effect on radical polymerization[11]. In our system however, we found that the molecular weight and molecular weight distribution of the block copolymer were affected by solvent as shown in *Table 1*.

Since the initiation mechanism for the binary system of BP and an aromatic amine[12,13] suggests exciplex formation via a one-electron transfer from the anilino group to BP under u.v. irradiation, then different routes might be followed in solvents with different polarities. In a non-polar solvent such as benzene (ε: 2.283 at 20°C), the nitrilo radical and binacol radical are easily formed by proton transfer from the anilino cation radical to the BP anion radical, and then the nitrilo radical initiates the

Table 1 Effect of solvent polarity on the CTP of VAc[a]

Sample	$PMMA_a$ ($\times 10^3$ mol l^{-1})	Conversion of VAc (%)	M_n ($\times 10^4$)	$\bar{M}_w/\bar{M}_n$
Benzene				
B_1	4.0	15	4.7	2.97
B_2	6.0	21	4.0	2.76
B_3	8.0	26	3.5	2.52
Acetonitrile				
A_1	4.0	14	4.8	2.99
A_2	6.0	19	4.0	2.77
A_3	8.0	24	3.5	2.54

[a] $[BP] = [PMMA_a]$; total volume: 10 ml; VAc: 5 ml; molecular weight of $PMMA_a$: 1.05×10^4; $\bar{M}_w/\bar{M}_n$: 1.34

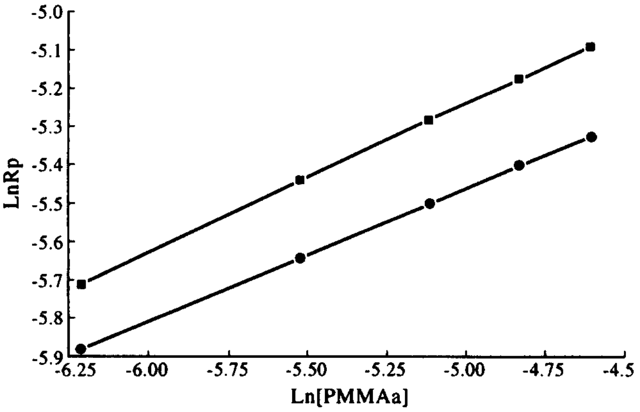


Figure 1 Dependence of R_p on the concentration of $PMMA_a$ (■, benzene; ●, acetonitrile)

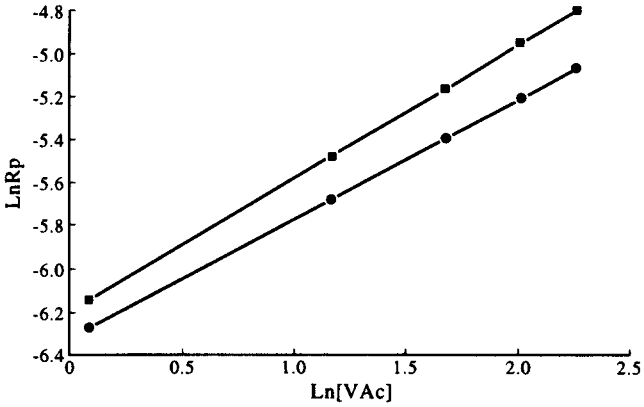


Figure 2 Dependence of R_p on the concentration of VAc (■, benzene; ●, acetonitrile)

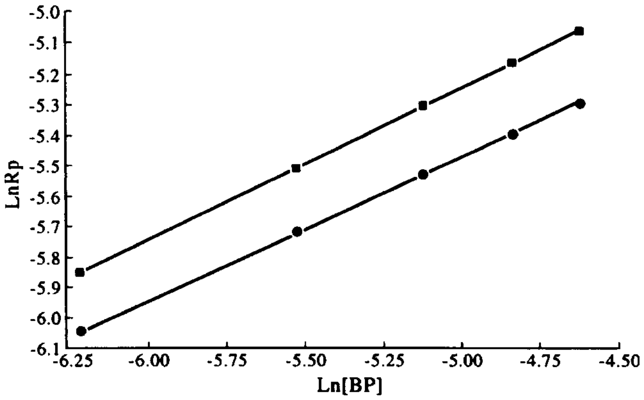


Figure 3 Dependence of R_p on the concentration of BP (■, benzene; ●, acetonitrile)

polymerization of VAc. However, in strongly polar solvents such as acetonitrile (ε: 37.5 at 20°C), the ion–radical pairs composed of BP and anilino may be solvated[14] as shown in *Scheme 4*, the initially tightly bound ion–radical pairs may become separated to form loose pairs, and thus proton transfer between them might be very difficult to carry out[15] owing to the increased distance between the species. This would lead to a decrease of the radical concentration, and so the conversion of VAc would decrease. However, the molecular weight of the copolymers in acetonitrile increases owing to the inverse dependence of molecular weight on concentration of the radical.

The kinetic expressions for block copolymerization in the different solvents were obtained from *Figures 1–3*, giving $R_p \propto [PMMA_a]^{0.39}[VAc]^{0.61}[BP]^{0.49}$ for benzene and $R_p \propto [PMMA_a]^{0.35}[VAc]^{0.55}[BP]^{0.49}$ for acetonitrile.

*Characterization of PMMA-**b**-***PVAc**

The purified diblock copolymer of PMMA-*b*-PVAc (run A_3 in *Table 1*) was characterized in detail by *FT*i.r., ^1H n.m.r. and g.p.c. *Figure 4* shows the strong bands at 1738 cm^{-1} attributed to the carbonyls of PMMA and PVAc. Resonances for hydrogen nuclei in the polymer at δ (ppm) of 0.88 (syndio-) and 1.02 (heterotactic) ($C-CH_3$), 1.82 ($-CH_2-$) and 3.60 ($-OCH_3$) for PMMA and 1.82 ($-CH_2-$), 2.03 (CH_3CO-) and 4.88 ($-CH-$) for PVAc are shown in *Figure 5a* and provide evidence supporting the existence of PMMA-*b*-PVAc.

Figure 6 shows g.p.c. data for the PMMA prepolymer (*Figure 6a*) and diblock copolymer of PMMA-*b*-PVAc (*Figure 6b*). For the former the molecular weight is about 10 500 and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$) is 1.34; for the latter there is only one peak with smaller retention volume, the molecular weight is about 35 300 and $\bar{M}_w/\bar{M}_n$ is 2.54.

*Hydrolysis of PMMA-**b**-***PVAc**

The hydrolysis of PMMA-*b*-PVAc was carried out in benzene with ethanolic sodium ethoxide as catalyst. In order to confirm whether the PMMA was hydrolysed simultaneously, quantitative analysis for the methoxy group in the PMMA block was conducted by n.m.r. The proton signal of α-substituted methyl with syndiotactic structure at 0.88 ppm in the PMMA block was used as internal standard and the variation in the peak area of methoxy at 3.60 ppm was measured. The results showed that the methoxy content after hydrolysis was nearly the same as before hydrolysis. After hydrolysis the proton signal arising from the methyl of the acetyl group at 2.03 ppm in the PVAc block had disappeared completely, and a new peak at 4.60 ppm, which was attributed to hydroxyl groups, appeared (see *Figure 5b*). Thus the selective hydrolysis of the PVAc block using sodium ethoxide as catalyst is quite successful.

CONCLUSIONS

The diblock copolymers of MMA and VAc were prepared by successive radical polymerization by using aniline–benzophenone as a photo-induced binary initiation system. The polarity of the solvent exerts an effect on the polymerization. In the formation of the second block unusual kinetic formulae were derived because of a decrease in the effective imino radical concentration, possibly due to entanglement of the imino end groups in the first block of PMMA in solution.

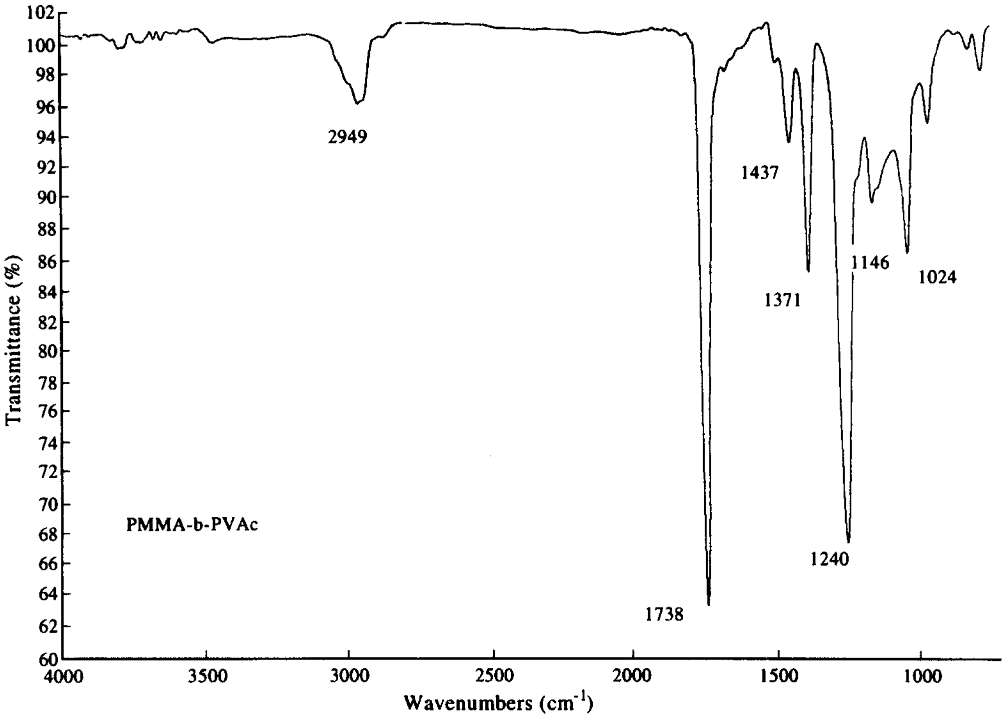


Figure 4 I.r. spectrum of PMMA-*b*-PVAc

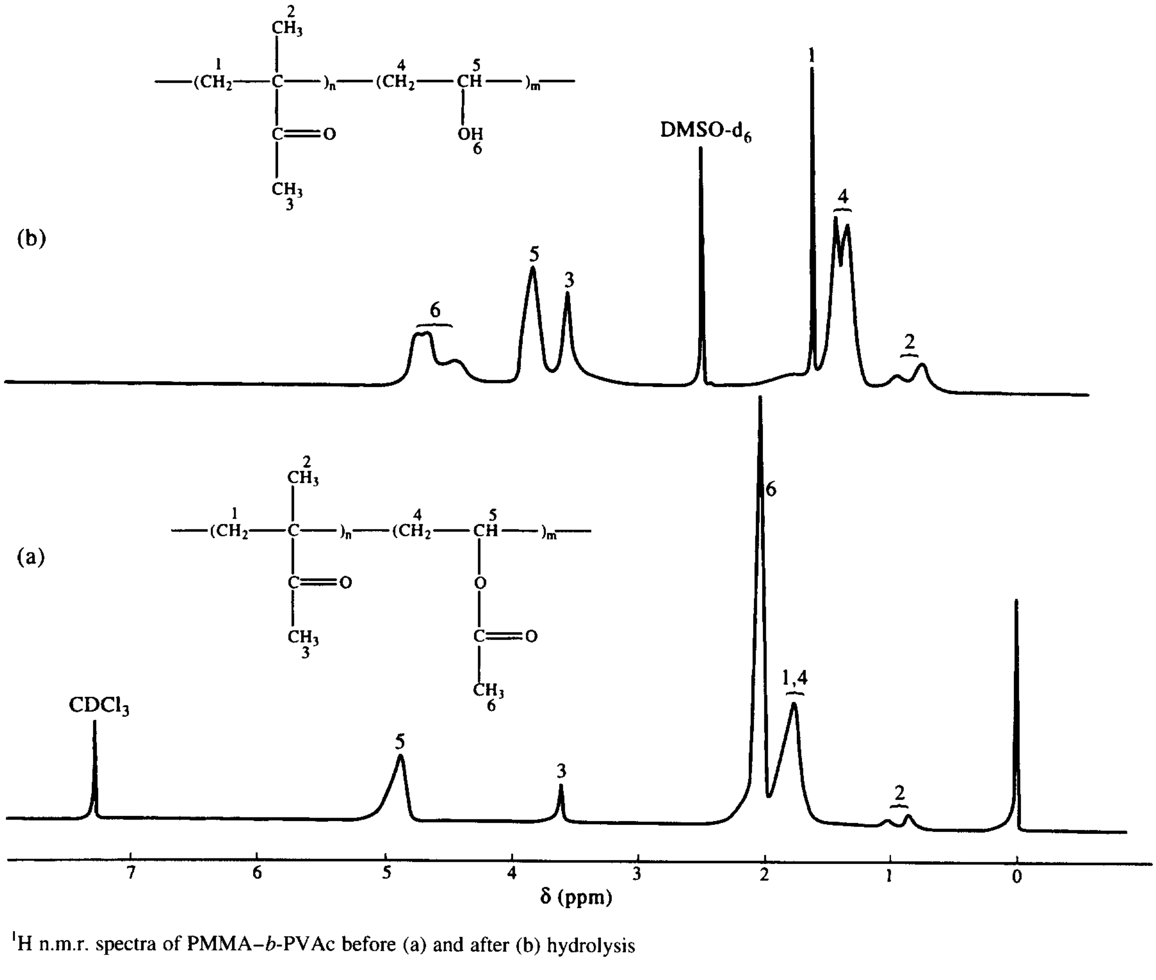


Figure 5 ^{1}H n.m.r. spectra of PMMA-*b*-PVAc before (a) and after (b) hydrolysis

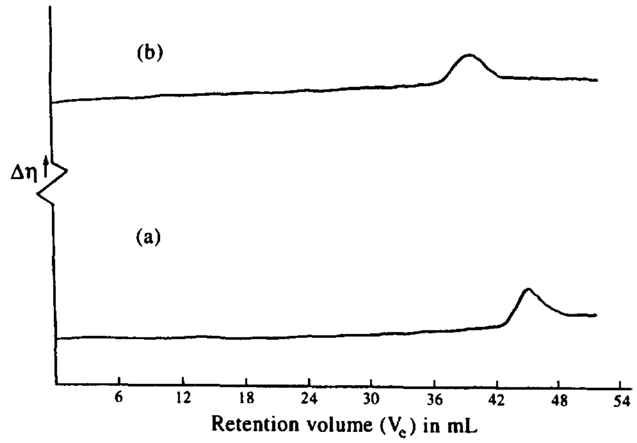


Figure 6 G.p.c. measurements of $PMMA_a$ precursor (a) and PMMA-*b*-PVAc (b)

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