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N.m.r. study of copolymer of styrene with methyl methacrylate prepared in presence of zinc chloride

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In the n.m.r. spectrum of a styrene (Sty)–methyl methacrylate (MMA) copolymer prepared in presence of zinc chloride at 60°C the phenyl protons of the styrene unit appeared as one peak at 3τ, the methoxy protons of methyl methacrylate unit appeared as three peaks at 6.4–6.8τ, 7.1–7.3τ and 7.5τ. The position of these peaks indicated an alternate copolymer. This was further confirmed by estimation of copolymer composition from n.m.r. spectrum and element analysis. The value of 'σ' which is the probability of alternating MMA and Sty units having same configuration was also determined and found to be 0.865 $\pm$0.006. It was found that the value of 'σ' was a direct function of concentration of zinc chloride.

Keywords Polymerization; nuclear magnetic resonance; styrene; methylmethacrylate; zinc chloride; analysis

Introduction

Nuclear magnetic resonance (n.m.r.) spectroscopy has been widely used for characterization of polymers. Ito[1,2] has determined structure, composition and stereochemistry of styrene methyl methacrylate copolymer prepared in presence of benzoyl peroxide and n-butyl lithium.

In this communication composition and stereochemistry of styrene-methyl methacrylate copolymer prepared in presence of zinc chloride has been determined.

Experimental

The methyl methacrylate, styrene monomers, Lewis acid (zinc chloride), initiator (azobis-isobutyronitrile, AIBN) were purified by standard methods[3]. The copolymerization reaction was carried out in a modified dilatometeric apparatus[3,4] under inert atmosphere of nitrogen gas at 60°C. The copolymer was precipitated with acidic methanol and was washed with acrylonitrile and cyclohexane to remove homopolymer and was dried to a constant weight.

The n.m.r. spectrum of the copolymer was taken on Perkin 100 M.C. spectrometer using CCl_4 as solvent and tetramethylsilane as internal reference.

Results and Discussion

The n.m.r. spectrum of copolymers prepared at 60°C in presence of 2×10^{-4} mol l^{-1} (*Figure 1*), 8×10 mol l^{-1} (*Figure 2*), 9×10^{-4} mol l (*Figure 3*) of zinc chloride showed following the characteristic peaks.

(i) One peak at 3τ due to phenyl protons of styrene unit.
(ii) Three separate peaks appeared at 6.4–6.8τ, 7.1–7.3τ, and at 7.5τ. These peaks are due to methoxy group of methyl methacrylate unit.
(iii) Three split peaks are present in the highest field

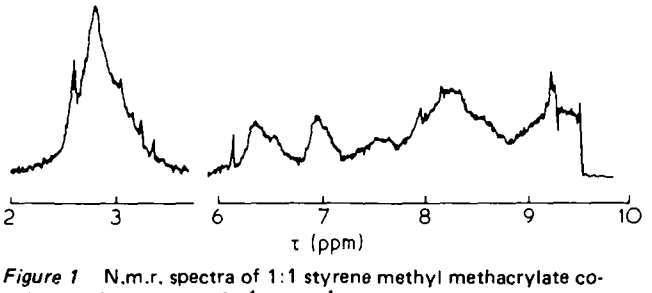

Figure 1 N.m.r. spectra of 1:1 styrene methyl methacrylate copolymer: $ZnCl_2 = 2 \times 10^{-4}$ mol l^{-1}, time = 2 h, AIBN = 2×10^{-4} mol l^{-1}, temperature = 60°C

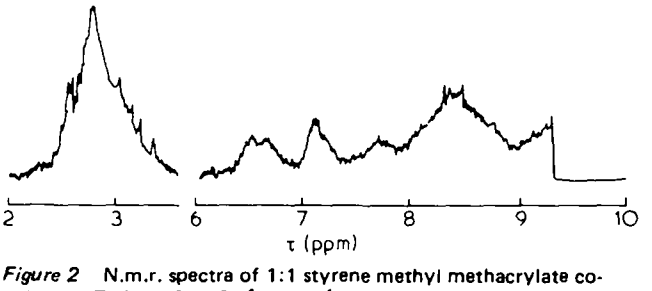

Figure 2 N.m.r. spectra of 1:1 styrene methyl methacrylate copolymer: $ZnCl_2 = 8 \times 10^{-4}$ mol l^{-1}, time = 2 h, AIBN = 2×10^{-4} mol l^{-1}, temperature = 60°C

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Table 1 MMA–Styrene copolymer composition estimated from peak area of methoxy protons of MMA by n.m.r. and element analysis

Concentration of zinc chloride (mol l^{-1}) x 10^4	Copolymer composition from element analysis				Copolymer composition from n.m.r. spectrum of copolymer		σ Calculated from n.m.r. spectrum
	Element percentage		MMA mol fraction	Sty. mol fraction	MMA mol fraction	Sty. mol fraction	
2	C = 78.5	H = 5.67	0.518	0.480	0.519	0.481	0.860
8	C = 77.2	H = 7.44	0.510	0.488	0.511	0.489	0.866
9	C = 76.8	H = 7.95	0.500	0.494	0.504	0.496	0.871

MMA = 0.1 mol l^{-1}
Sty = 0.1 mol l^{-1}
AIBN = 2 x 10^{-4} mol l^{-1}
Temperature = 60°C
Polymerization time = 120 min

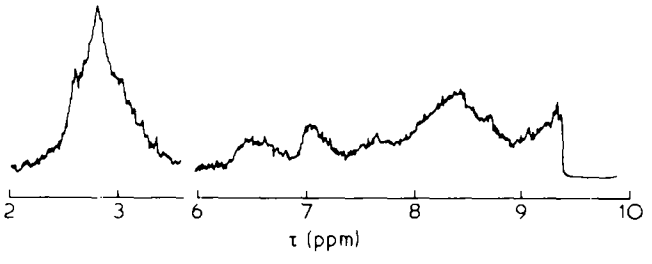
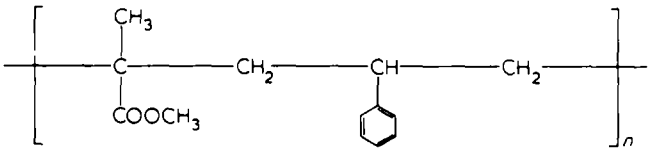


Figure 3 N.m.r. spectra of 1:1 styrene methyl methacrylate co-polymer: $ZnCl_2$ = 9 x 10^{-4} mol l^{-1}, time = 2 h, AIBN = 2 x 10^{-4} mol l^{-1}, temperature = 60°C

of 8.8–9.5τ which is due to α-protons of methyl group of methyl methacrylate unit.

On the basis of presence of these peaks in the spectrum, it is concluded that a styrene–methyl methacrylate copolymer is obtained.

Determination of structure of copolymer. (i) The n.m.r. spectrum of copolymers showed that the methoxy protons of methyl methacrylate (MMA) unit appear as three separate peaks at 6.4–6.8τ, 7.1–7.3τ and at 7.5τ and phenyl protons of styrene unit appears as a single peak at 3τ which shows that the copolymer has an alternate arrangement of styrene and methyl methacrylate units, because in case of random copolymer the methoxy protons of the MMA unit appear as one broad peak at 6.4τ and the phenyl protons of styrene unit appear as two peaks at 2.9τ and 3.4τ[2]. Thus it can be concluded that when styrene has been copolymerized with methyl methacrylate in presence of zinc chloride, an alternate copolymer with the following structure has been prepared:



Estimation of copolymer composition. The composition of the copolymer was estimated from the peak area of various peaks using the following equations given by Ito:

$$X + Y + Z = P_1[M] = 1 - P_1[S]$$

where X—area of peak at 6.4–6.8τ; Y—area of peak at 7.1–7.3τ; Z—area of peak at 7.5τ; $P_1[M]$—mol fraction of methyl methacrylate unit in copolymer; $P_1[S]$—mol fraction of styrene unit in copolymer.

The area of peak was calculated by the integration method given by Morrison[5] and the copolymer composition is listed in *Table 1*. It was found that when system contained 2 x 10^{-4} mol l^{-1} of zinc chloride the mol fraction of styrene in the copolymer was found to be 0.481. However, when the concentration of zinc chloride was increased to 9 x 10^{-4} mol l^{-1} the mol fraction of styrene in the copolymer was increased to 0.496. This copolymer composition is also in agreement with that calculated from element analysis of the copolymer (*Table 1*). This copolymer composition also explains the alternate structure of the copolymer.

Stereochemistry of copolymer. The stereochemistry of the copolymer was determined by calculating the term σ^1 which is the probability of alternating MMA and styrene units having same configuration, with the help of equations (2), (3) and (4) given by Ito[1].

$$Z = \sigma^2 P_3[SMS] \quad (2)$$

where $P_3[SMS]$ is the triad concentration of the polymer which was calculated with the help of equation (3)

$$P_3[SMS] = P_1[M] P_{MS}^2 \quad (3)$$

where P_{MS} is the probability of a given M unit being followed by an S unit, and can be calculated with the help of equation (4):

$$P_{MS} = \frac{1}{(1 + r_m X)} \quad (4)$$

where r_m = monomer reactivity ratio; X = mol ratio of styrene to methyl methacrylate. The value of r_m was taken as 0.5[1] and the mol ratio of styrene to methyl methacrylate was calculated from n.m.r. as shown in *Table 1*.

The value of σ for a copolymer of MMA–styrene prepared in absence of a Lewis acid has been found to be 0.5[1]. However the value of σ increases, as shown in *Table 1*, to 0.860 when 2 x 10^{-4} mol l^{-1} of zinc chloride was added to the system. When the concentration of zinc chloride was increased to 9 x 10^{-4} mols the value of σ was increased to 0.871. This shows that zinc chloride favours the alternate placement of MMA and styrene units having the same configuration.

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