Carbon – 13 NMR relaxation studies of methyl methacrylate – n-butyl methacrylate copolymers

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Methyl methacrylate – n-butyl methacrylate copolymers of different compositions have been prepared at 70°C, using benzoyl peroxide as an initiator. Proton decoupled ^{13}C NMR spectra of the samples have been recorded and spin lattice relaxation times (T_1) measured using FIRFT method. Effect of copolymer composition on the T_1 values has been discussed.

Nuclear magnetic resonance has been extensively applied to the complex dynamic problems presented by polymer chains. Carbon-13 NMR spin lattice relaxation measurements represent a powerful method for investigating molecular motion in polymers. Information about backbone motion and segmental internal rotation in polymers can be obtained from measurements of ^{13}C-spin lattice relaxation times (T_1s) and nuclear Overhauser effects (NOEs)[1-4]. The dependence of the T_1s and NOEs on the strength of the magnetic field, temperature and solvent have been reported by several investigators[5-8]. Various models have been developed in order to interpret spin lattice relaxation data for main chain and side chain carbons in polymers[9-13]. The simplest is the rigid isotropic model which is characterised by single correlation time[9]. Levy and Wang[8] have reported the effect of solvent on the motion of main chain and side chain carbons in poly (n-butyl methacrylate). A literature survey reveals that no work so far has been reported on the ^{13}C NMR relaxation studies of methyl methacrylate – n-butyl methacrylate copolymers, and hence the title investigation.

Materials and Methods

Methyl methacrylate – n-butyl methacrylate copolymers of varying compositions were prepared at 70°C using benzoyl peroxide as an initiator.

Proton decoupled ^{13}C NMR spectra were recorded in $CDCl_3$ at 25°C on a 25 MHz Jeol FX-100 NMR spectrometer; chemical shifts are expressed in δ ppm downfield from TMS. Free induction decays were accumulated with 8K data points. T_1 measurements were performed using,

the (τ-180°-t-90°)x fast inversion recovery pulse sequence (FIRFT). A total of 1Lt values ranging from 0.01 to 20s were used to obtain a given T_1 data set. A least mean square analysis performed by the computer gave the reported T_1 values. Polymer solutions were deoxygenated by bubbling pure nitrogen through the samples. Molecular weights of the copolymers were determined by viscometry in chloroform at 30°C.

Results and Discussion

A representative proton decoupled ^{13}C NMR spectrum of methyl methacrylate – n-butyl methacrylate copolymer is shown in Fig.1. Assignments of various carbon resonance signals have been made by comparing the ^{13}C NMR spectrum of copolymer with those of poly(methyl methacrylate) and poly(n-butyl methacrylate). Chemical shifts of various carbon atoms on the copolymer (structure **1**) are: δ177.58 (C=O), δ64.57 (C-1), δ54.19 ($-CH_2-$), δ51.47 (OCH_3), δ44.97, δ44.55 (quaternary carbons), δ30.07 (C-2), δ19.16 (C-3), δ18.38 (C-CH_3), δ16.38 ($-*CH_3$) and δ13.57 (C-4).
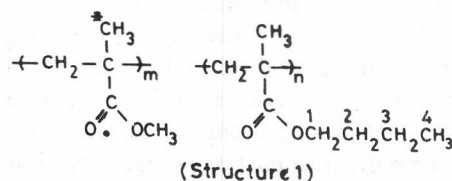
(Structure 1)

Copolymer composition, comonomer reactivity ratios and microstructure of this copolymer system has been described in our earlier publication[14] and it has been observed that the chemical shifts for various carbons are not affected by the
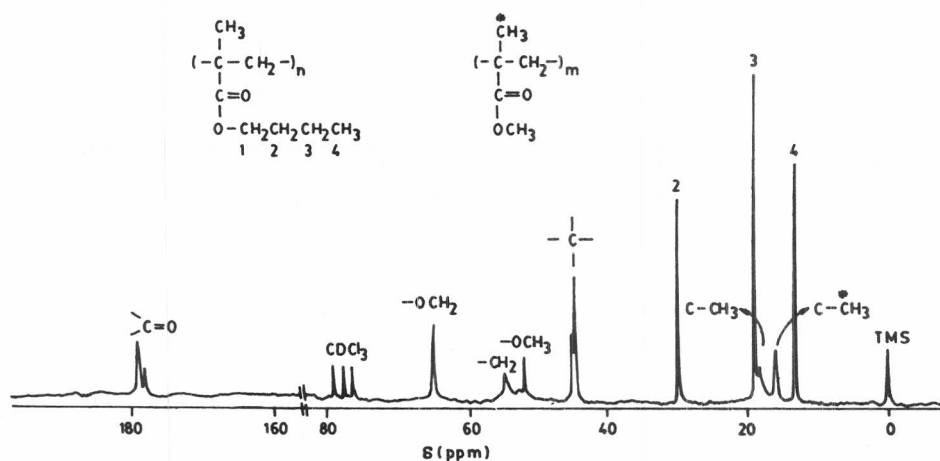
Fig. 1—25 MHz proton decoupled ^{13}C NMR spectrum of methyl methacrylate-n-butyl methacrylate copolymer in CDCl$_3$ at 25°C

Table 1 — Spin lattice relaxation time (T$_1$) data for methyl methacrylate − n-butyl methacrylate copolymers

MMA (mol %)	Mol wt (M × 10^{-5})	T$_1$ (s)							
		C-1	C-2	C-3	C-4	-C̣-	-OCH$_3$	>C=O	-CH$_2$
30.0	4.26	0.06	0.31	0.83	1.75	0.50	0.69	0.77	—
40.0	4.34	0.14	0.40	1.03	2.15	0.40	0.40	0.85	—
50.0	4.30	0.05	0.33	0.53	0.95	0.37	0.27	1.10	—
60.0	4.70	—	0.25	0.77	1.77	0.53	0.37	1.11	0.07
70.0	4.20	—	0.33	0.77	—	0.54	0.24	0.80	0.08

copolymer composition, only the peak intensities are affected.

Carbon-13 spin lattice relaxation times (T$_1$s) for various carbon atoms in the copolymer chain are given, for all the copolymer samples in Table 1. The T$_1$ value of the methylene carbon is very low due to the two directly attached protons and the relaxation is dominated by the dipole - dipole mechanism[3]. In the n-butyl side chain of n-butyl methacrylate unit, the value of T$_1$ increases from C-1 to C-4. This trend is observed in all the copolymer samples. The molecular anchor at oxygen of the ester group does restrict the motion of C-1, resulting in the long correlation time (τ_c) and small value of T$_1$. Methylene carbons in the side chain, i.e. C-2 and C-3 show appreciable segmental motion resulting in their high values of T$_1$. The methyl carbon in the side chain has a large degree of internal motion, resulting in the highest value of T$_1$ amongst the four carbons in the side chain.

The values of T$_1$ for the side chain carbons and methylene carbons are in good agreement with those given for poly (n-butyl methacrylate) by Levy and Wang[8]. Small variations may be due to the use of different solvents and magnetic field during the NMR measurements. The low value of T$_1$ for quaternary carbon indicates that the dipo-lar spin relaxation must arise from nearby protons[8]. The triad sequence concentration seems to affect the T$_1$ value of quaternary carbon. The T$_1$ value is the least for copolymer containing 50 mole per cent of methyl methacrylate and increases on either side of this concentration. In our earlier publication[14], we have shown that at 50% methyl methacrylate, the concentration of 112(211) and 221(122) triad (where 1 = methyl methacrylate and 2 = n-butyl methacrylate) is maximum and decreases on either side of this concentration. The maximum concentration of 112 and 221 triads corresponds to minimum T$_1$ value for the quaternary carbon.

To the best of our knowledge, Mark-Houwink constants for this copolymer system have not been reported, therefore we have taken these constants as equal to that for poly (methyl methacrylate) from the literature[15]. Mark-Houwink constants are: $K = 4.3 \times 10^{-3}$ ml/g, and $a = 0.80$. The molecular weights are given in Table 1. The values of molecular weights are in the order of million for all the samples.

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