Analysis of the stereochemistry of poly(2,3-epoxypropyl methacrylate) by 75 MHz ^{13}C n.m.r. spectroscopy

Pradeep K. Dhal*†‡, G. N. Babu* and Alois Steigel†
**Department of Chemistry, Indian Institute of Technology, Powai, Bombay 400 076, India*
†Institute of Organic and Macromolecular Chemistry, University of Düsseldorf, D-4000, Düsseldorf 1, FRG
(Received 25 October 1988; accepted 18 January 1989)

The tacticity of poly(2,3-epoxypropyl methacrylate) has been analysed. For detailed elucidation of stereochemical features, polymers with varying degrees of tacticities were synthesized by anionic and free radical polymerization. Using two-dimensional ^{13}C–^{1}H correlation, signal assignments to different carbon atoms have been made. Using the peak multiplicities for carbonyl carbon atom resonance, in particular, tacticity assignments up to the pentad level have been achieved. The validity of sequence assignments has been tested and confirmed by calculated values from statistical relationships. While the anionically polymerized sample in toluene obeys a first-order Markov type chain growth process, the chain propagation for free radical polymer and anionic polymer in THF has been found to be Bernoullian.

(Keywords: stereochemistry; n.m.r. spectroscopy; polymerization)

INTRODUCTION

Investigation of the stereochemical features of vinyl polymers (the so-called tacticity) and their correlation with the physicochemical and physicomechanical properties of polymers is an important goal in contemporary polymer research[1]. For the elucidation of these microstructural features, high resolution nuclear magnetic resonance (n.m.r.) spectroscopy, particularly ^{13}C n.m.r., has emerged as one of the most powerful tools. Due to wide chemical shift dispersions and extreme sensitivity to chain stereochemistry, this technique yields valuable information on chain structures for longer stereosequences[2,3].

In recent years remarkable progress has been made in analysing stereostructures of several well known polymers, namely poly(methyl methacrylate)[4], polystyrene[5], polypropylene[6] etc., with the help of ^{13}C n.m.r. The n.m.r. literature on the identification of the microstructures of these polymers is now extensive and has been repeatedly reviewed[7–9]. On the other hand, such studies on polymers based on functional vinyl monomers have been done less frequently. Difficulties in unequivocal assignments of signals to different carbon atoms in the multicarbon monomeric units in these polymers, possible signal overlapping and/or unavailability of appropriate models are possible factors contributing to the small number of research reports on the structural analysis of these polymers. The need for functional polymers for several specialty applications demands the synthesis of these materials with well controlled structure and topologies[10,11].

The homopolymer and copolymers based on 2,3-epoxypropyl methacrylate belong to the class of potential functional polymers. The high reactivity of the epoxy group to large varieties of reagents provides novel routes to prepare numerous multifunctional polymers through chemical modification of these polymers[12,13]. Thus these polymers have found extensive applications as polymeric reagents, carriers for immobilization of enzymes and supports for affinity chromatography as well as in microelectronics research[14–18]. Some time ago we reported the results of ^{13}C n.m.r. analysis of the microstructure of poly(2,3-epoxypropyl methacrylate) prepared by free radical initiation and monomer sequence analysis of its copolymers with several alkyl acrylates at 25 MHz[19,20]. To validate and refine our previous tacticity assignments, as well as to identify tacticities at longer stereosequences, we have reinvestigated this polymer. Towards this end, we have synthesized different types of this polymer with varying degrees of tacticity through anionic polymerization. Furthermore, n.m.r. measurements at higher magnetic field (75 MHz for ^{13}C nuclei) brought about improved spectral resolution, enabling us to assign signals due to longer stereosequences more accurately. The present paper describes the results of this study.

EXPERIMENTAL

Materials

The polymerization solvents, THF and toluene, were obtained from E. Merck as reagent grade chemicals. The solvents were purified by a two-step procedure involving an initial distillation under nitrogen from finely dispersed sodium followed by vacuum condensation from diphenylhexyl lithium and stored under argon atmosphere.

---

‡ To whom correspondence should be addressed.
Now at: Division of Polymer Chemistry, National Chemical Laboratory, Pune-411 008, India

0032-3861/89/081530-06$03.00

1,1-Diphenyl ethylene, obtained from Fluka AG, was used after distillation under reduced pressure. n-Butyl lithium was obtained from E. Merck as 1.6 M solution in hexane and was used as received. 2,2-Azo-bis-isobutyronitrile (AIBN), obtained from Fluka AG, was purified by recrystallization from ethanol before use. 2,3-Epoxypropyl methacrylate (E. Merck) was first distilled from finely powdered CaH_2 and was further distilled under reduced pressure immediately before polymerization.

Polymerization

Anionic polymerization. These reactions were performed under an argon atmosphere in a scrupulously clean and dry double-walled glass reactor (100 ml capacity) connected to a Lauda automatic ultracryostat system. The polymerization solvent was transferred, via a dry glass syringe under a positive pressure of argon, to the clean reaction vessel fitted with a silicon rubber septum, followed by the calculated amount of diphenyl ethylene. The reactor was cooled to -78°C. To this solution 1.1 mol excess (with respect to diphenyl ethylene) of n-butyl lithium was added through the syringe. The red anion of the diphenylhexyl lithium was generated. Subsequently, a predetermined amount of the purified monomer was slowly added. Initiation was rapid, as could be observed from the quick disappearance of the red colour. After polymerizing for 6–8 h, the living polymers were terminated at -78°C with pure methanol. The polymers were isolated by repeated dissolution and reprecipitation from chloroform and methanol, respectively, and were finally dried to constant weight at 50°C under reduced pressure.

Free radical polymerization. The monomer was polymerized in bulk at 60°C using AIBN as free radical initiator (1 wt% monomer). The monomer initiator mixture was made oxygen free by repeated cool–thaw cycling from -78°C (dry ice–acetone) and was polymerized under dry nitrogen. The polymerization reaction was quenched by pouring the mixture into an excess of petroleum ether (40–60°C). The purification and isolation procedure used was the same as for anionic polymerization.

N.m.r. measurements

High resolution 75 MHz ^{13}C n.m.r. spectra were recorded with a Varian VXR-300 spectrometer. Measurements were made at 50°C in $CDCl_3$ (20% wt/vol solution) using TMS as internal reference. The spectra were obtained using 75° pulse and WALTZ decoupling. The peak areas measured after deconvolution (when necessary) were used for the estimation of relative peak intensities. The reported results are an average of three measurements of peak intensities which vary within $\pm 3\%$.

Two-dimensional (2D) ^{13}C–^1H correlated spectroscopy was performed using the following standard pulse sequence[21]: ^1H:RD–90°–$(t_1+\Delta_1)$–90°–Δ_2–decouple; ^{13}C:RD–$t_1/2$–180°–$t_1/2$–Δ_1–90°–Δ_2–detect. The 2D ^{13}C–^1H correlated spectrum thus obtained maps the directly attached protons and carbon signals.

RESULTS AND DISCUSSION

An unbiased assignment of ^{13}C n.m.r. signals to different stereosequences pertaining to chain configuration requires synthesis of polymers of different tacticities. By comparing the experimental results with the calculated values, tacticity assignments can be made with sufficient accuracy. Anionic polymerization of 2,3-epoxypropyl methacrylate using 1,1-diphenylhexyl lithium as initiator furnishes polymers whose tacticity (contents) depends on the nature of polymerizing solvents. This initiator system has been found to be very selective for vinyl double bond and does not interfere with the ester group[22]. Thus, by polymerizing this monomer in toluene and THF, it becomes possible to obtain isotactic- and syndiotactic-enriched polymers, respectively.

A representative ^{13}C n.m.r. spectrum for the isotactic-enriched sample is depicted in *Figure 1*. Some of the peak assignments in our previous report[19] were incorrect due to signal overlapping at low field. The resonance lines at 52 ppm and 52.5 ppm, previously

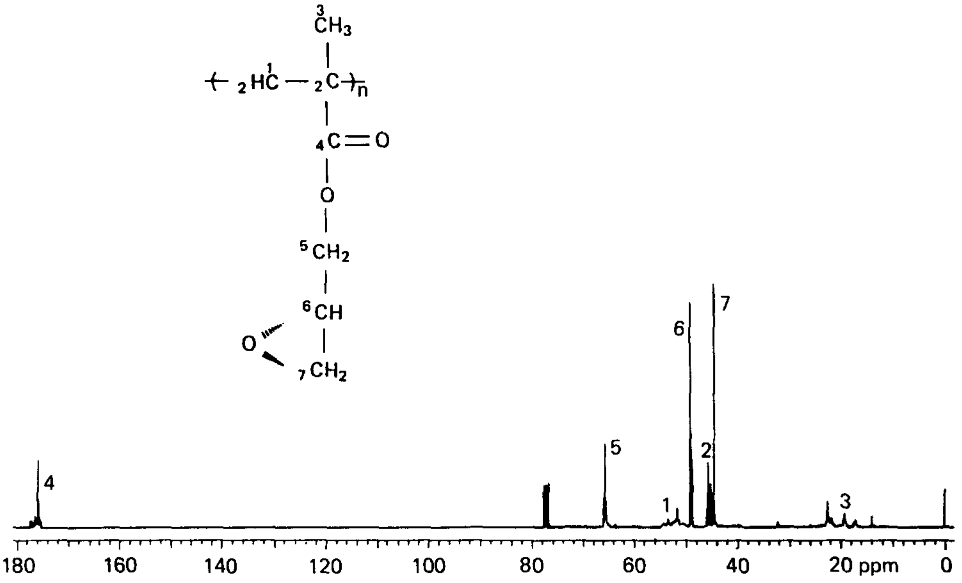

Figure 1 75 MHz ^{13}C n.m.r. spectrum of isotactically enriched poly(2,3-epoxypropyl methacrylate)

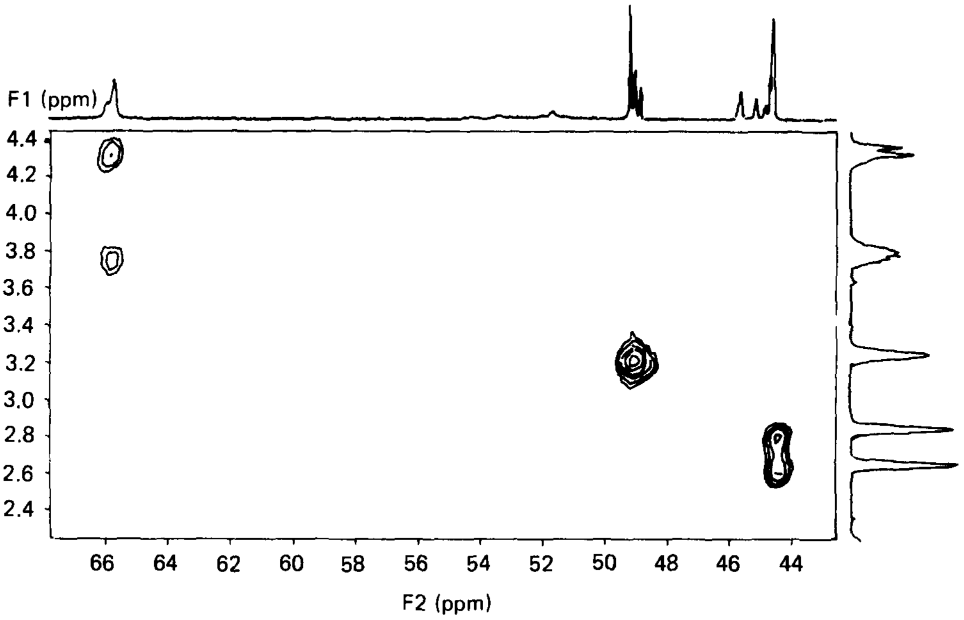

Figure 2 75 MHz ^{13}C–^{1}H Hetero-COSY spectrum of isotactically enriched poly(2,3-epoxypropyl methacrylate)

assigned to the epoxy $-OCH_2$ (C-7) and epoxy methine $-OCH$ (C-6) carbon atoms, are due to the main chain methylene carbon atom. Furthermore, better signal dispersions revealed that the high field peak of the 44.5–46 ppm region, previously assigned to the syndiotactic part of the backbone quaternary carbon atom, is instead due to the epoxy $-OCH_2$ (C-7) carbon atom. Finally, the signal at 49 ppm is now reassigned to the epoxy methine $-OCH$ (C-6) carbon atom. The intensity patterns for the polymers with differing degrees of tacticity confirm these assignments. The authenticity of the present assignments is also supported by 2D ^{13}C–^{1}H heteronuclear correlation experiments, which map the connectivity between directly bonded ^{13}C and ^{1}H nuclei[23]. The 2D-correlation contour plot of the isotactic-enriched sample for the region of interest is shown in *Figure 2*. As can be clearly seen, the proton signals of the epoxy methylene unit between 2.4 and 2.8 ppm correlate with the carbon signal at 44.6 ppm due to the corresponding carbon atom (C-7), and the epoxy methine proton resonance at ≈ 3.2 ppm correlates with the carbon signal at ≈ 49 ppm due to the C-6 carbon atom, thus validating our signal assignments.

After establishing the assignments of resonance lines to different carbon atoms, we made a tacticity analysis of this polymer. As is evident from the n.m.r. trace, virtually every carbon atom reveals its sensitivity to main chain configurations. We attempted to do the microstructural analysis using all these signals. Although, in general, some of the assignments appear obvious, by inspecting the intensity patterns of the resonance lines for different polymers with varying tacticity contents, a more careful analysis was required for rational configurational assignments. Thus, a combination of experimental results and calculated data was necessary for unequivocal assignments, particularly for longer stereosequences.

The methylene carbon atom in the main chain reveals sensitivity to longer stereosequences (possibly hexads) (*Figure 3*), but peak resolution was inadequate for structural analysis. The quaternary carbon atom (*Figure 4*) shows distinct triad sensitivity with possible pentad indications. The α-methyl carbon atom and carbonyl carbon atom, as shown in *Figures 5* and *6*, reveal distinct structural sensitivity at the pentad level. The best resolution is observed for the carbonyl carbon atom, which has been used for systematic analysis.

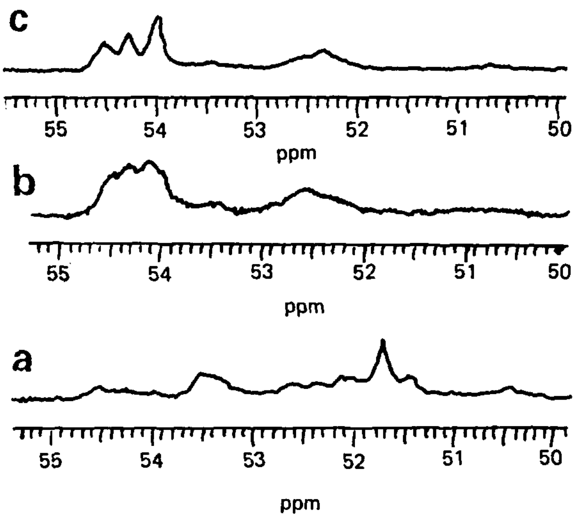

Figure 3 Backbone methylene region of ^{13}C n.m.r. spectra of different samples of poly(2,3-epoxypropyl methacrylate) prepared by: (a) anionic polymerization in toluene; (b) anionic polymerization in THF; (c) free radical polymerization

The three distinct peaks of the backbone quaternary carbon atom have been assigned to syndiotactic, heterotactic and isotactic triads, from upfield to downfield, respectively. The relative intensities of different triads for individual polymers were determined from the measurements of peak areas. With the help of these data, it becomes possible to evaluate the mechanisms of chain propagation, i.e. Bernoullian or Markov type chain growth, under different polymerization conditions. By using well known relationships[24,25] between the triad data and probability factors, the chain growth mechanism can be conveniently

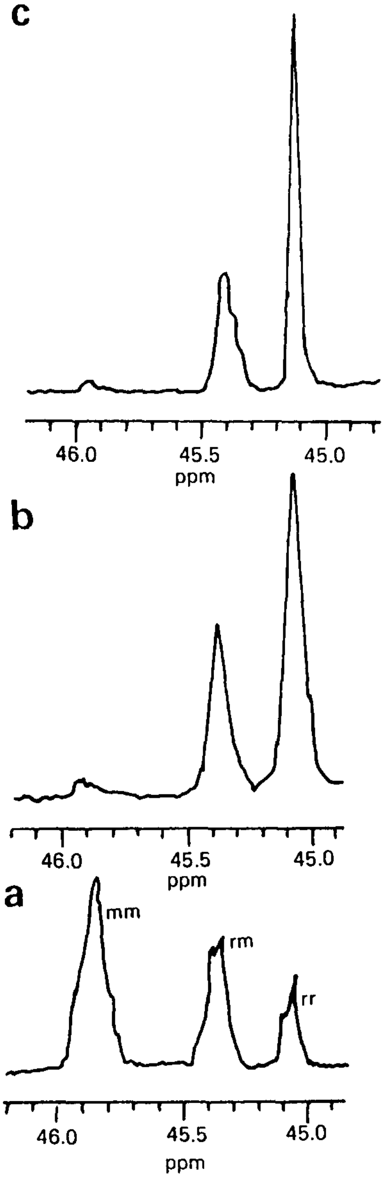

Figure 4 Backbone quaternary carbon region of ^{13}C n.m.r. spectra of different samples of poly(2,3-epoxypropyl methacrylate) prepared by: (a) anionic polymerization in toluene; (b) anionic polymerization in THF; (c) free radical polymerization

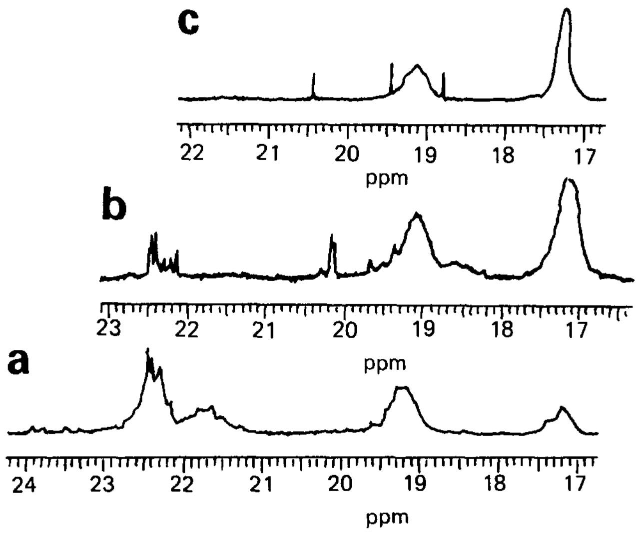

Figure 5 α-Methyl carbon region of ^{13}C n.m.r. spectra of samples of poly(2,3-epoxyproply methacrylate) prepared by: (a) anionic polymerization in toluene; (b) anionic polymerization in THF; (c) free radical polymerization

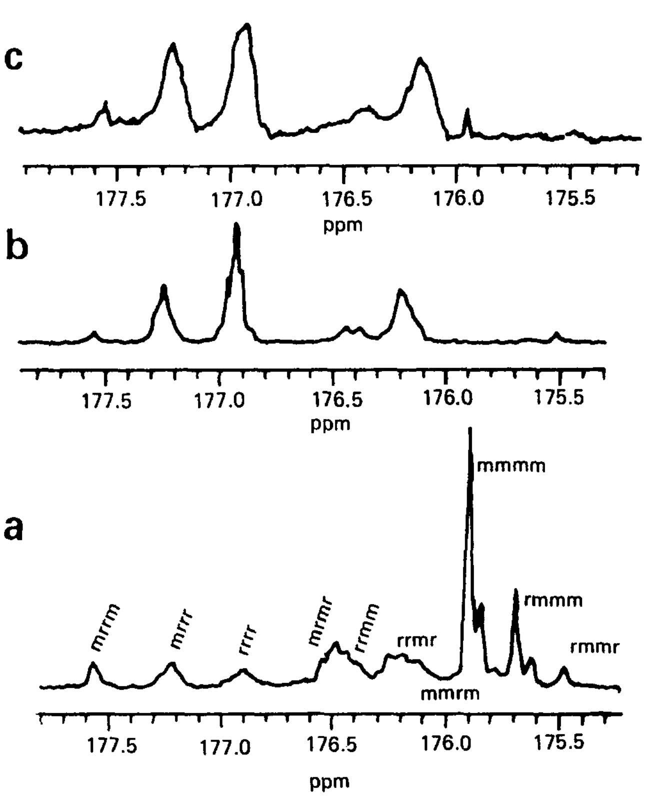

Figure 6 Carbonyl carbon region of ^{13}C n.m.r. spectra of samples of poly(2,3-epoxypropyl methacrylate) prepared by: (a) anionic polymerization in toluene; (b) anionic polymerization in THF; (c) free radical polymerization

deduced. $P_{(m/r)} = 1 - P_{(m/m)}$ is the probability that a racemic follows a meso placement and $P_{(r/m)} = 1 - P_{(r/r)}$ is the probability that a meso follows a racemic addition. If the sum $P_{(m/r)} + P_{(r/m)} = 1$, the chain growth process is Bernoullian and only one probability $P_{(m)}$ or $P_{(r)}$ is required. Any deviation from such a situation is indicative of Markov type chain propagation. The results on these triad tacticity data along with the probability values are summarized in *Table 1*.

As expected, the stereorandom polymer obtained by free radical initiation obeys the Bernoullian chain propagation mechanism. Anionically initiated polymer obtained in toluene possesses a high proportion of isotactic structures and follows a first-order Markov process. Anionic polymerization of this monomer in THF medium does not appear to control chain stereoregulation, since the experimental results on triad data for this polymer fit more closely to the Bernoullian model. For the latter case, the ion pair may exist as free ions to facilitate the addition of incoming monomer to the growing macroanion.

The carbon atom resonance appearing over the chemical shift range of 175.5–177.8 ppm (*Figure 6*) shows several multiplets suggestive of its sensitivity to longer-range tacticity effects. This enabled assignment of the signals to different possible pentad sequences (for certain pentads, heptad sensitivity is indicated). The three peaks in the upfield region were assigned to the isotactic-type pentads and those in the downfield region assigned to the syndiotactic-type pentads. Accordingly, the remaining peaks are due to different possible heterotactic pentads. These assignments appear quite reasonable since the signal intensities vary in accordance with the tacticity content of the polymers. These

Table 1 Triad tacticity data for three different poly(2,3-epoxypropyl methacrylate) samples based on main chain quaternary carbon atom ^{13}C resonance

	Rel. Conc. of different triads					
Samples[a]	mm	mr+rm	rr	$P_{m/r}$	$P_{r/m}$	$P_{m/r}+P_{r/m}$
A	0.53	0.32	0.15	0.23	0.52	0.75
B	0.04	0.32	0.64	0.80	0.20	1.00
C	0.06	0.36	0.58	0.75	0.23	0.98

[a] A, Prepared by anionic polymerization in toluene. B, Prepared by anionic polymerization in THF. C, Prepared by free radical polymerization

Table 2 Pentad level tacticity assignments from carbonyl carbon atom resonance of poly(2,3-epoxypropyl methacrylate) obtained by free radical polymerization

Pentad designation	Chemical shifts (ppm)	Relative peak intensity	
		found	calculated[a]
rmmr	175.48	0.027	0.033
rmmm	175.63	0.018	0.021
mmmm	175.80	0.003	0.003
mmrm	175.96	0.022	0.021
rrmr	176.15	0.228	0.211
rrmm	176.45	0.076	0.066
rmrm	176.52	0.061	0.066
rrrr	176.93	0.312	0.333
mrrr	177.25	0.212	0.211
mrrm	177.56	0.041	0.033

[a] Calculated using $P_m=0.24$

Table 3 Pentad level tacticity assignments from carbonyl carbon resonance of poly(2,3-epoxypropyl methacrylate) obtained by anionic polymerization in toluene (sample A) and THF (sample B)

Pentad designations	Chemical shifts (ppm)	Relative peak intensity	
		Sample A	Sample B
rmmr	175.48	0.022	0.028
rmmm	175.62–175.68	0.141	—
mmmm	175.84–175.9	0.311	—
mmrm	176.08	0.071	0.25
rrmr	176.18	0.086	—
rrmm	176.42	0.082	0.048
rmrm	176.54	0.108	0.072
rrrr	176.92	0.052	0.358
mrrr	177.22	0.078	0.203
mrrm	177.57	0.041	0.032

assignments of tacticity are in agreement with our previously reported results[19]. The assignments are further verified by calculating the individual pentad fractions using statistical methods, which confirms the assignments. For the atactic polymer, with the Bernoullian probability factor ($P_m=0.23$) obtained from the quaternary carbon resonance, the intensities of different possible pentad structures were calculated. The experimental and calculated values are summarized in *Table 2*. Close agreement between these results attests to the reliability of the tacticity assignments.

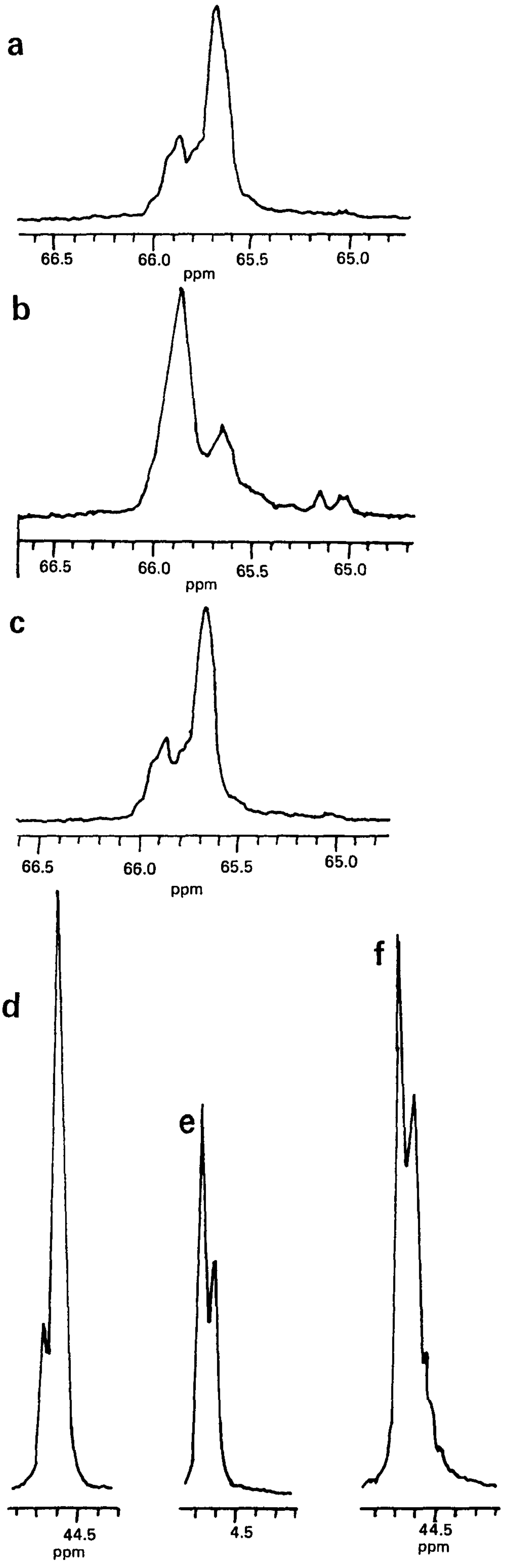

Figure 7 (a)–(c), Epoxy methylene and (d)–(f), ester methylene carbon regions of ^{13}C n.m.r. spectra of samples of poly(2,3-epoxypropyl methacrylate) prepared by: (a), (d) anionic polymerization in toluene; (b), (e) anionic polymerization in THF; (c), (f) free radical polymerization

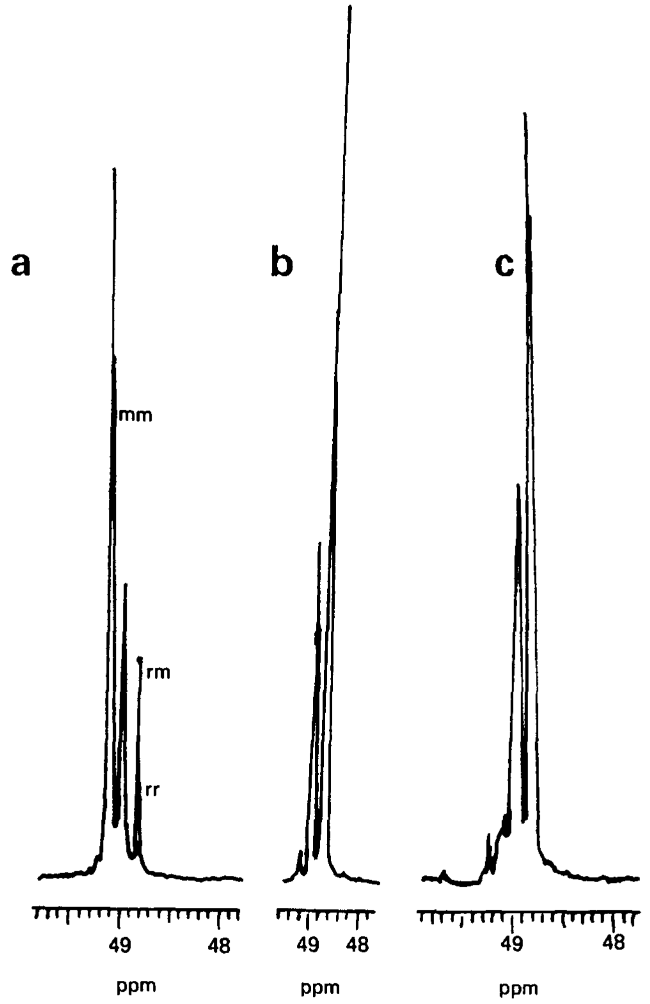

Figure 8 Epoxy methine carbon region of ^{13}C n.m.r. spectra of samples of poly(2,3-epoxypropyl methacrylate) prepared by: (a) anionic polymerization in toluene; (b) anionic polymerization in THF; (c) free radical polymerization

For the isotactically enriched polymer, it is necessry to use Markov statistics to confirm the assignment. For a first-order Markovian process, the following relationships can be utilized to test the precision of the tacticity analysis[26]:

$$\mathrm{mmmr} + 2(\mathrm{rmmr}) = \mathrm{mmrm} + \mathrm{mmrr} \qquad (1)$$

$$\mathrm{mrrr} + 2(\mathrm{mrrm}) = \mathrm{rrmr} + \mathrm{rrmm} \qquad (2)$$

These are very strategic equations and are pertinent to testing the validity of pentad assignments. Furthermore, these equations are independent of chain growth mechanisms and can be applied to both Bernoullian and Markovian types of propagation processes. The experimental results, summarized in *Table 3* obey these relationships (equations (1) and (2)) quite well, thus confirming the structural assignments.

Interestingly, all the side chain carbon atoms belonging to the 2,3-epoxypropyl group show sensitivity to chain stereochemistry. At first it may be expected that, due to the presence of a chiral centre (epoxy methine C atom), all three carbon atoms would show multiple signals owing to diastereomerism. But, on the contrary, the intensity of these multiple lines varies as a function of stereoregularity of the polymer chain. Nevertheless, the possibility of diastereomeric splitting cannot be completely ruled out. The tacticity assignments for the two methylene carbon atoms appearing at 44.6–44.8 and 65.6–65.9 ppm (*Figure* 7) are unclear. The methine carbon atom of the epoxide ring reveals three sharp signals at 48.82, 48.98 and 49.12 ppm, as can be seen from *Figure 8*. These lines are unequivocally assignable to syndiotactic, heterotactic and isotactic triad components, respectively.

CONCLUSIONS

The structural and stereochemical features of poly(2,3-epoxyproply methacrylate) have been systematically elucidated. With the help of 2D ^{13}C–^{1}H correlation spectroscopy, the uncertainty of signal assignments to different carbon atoms has been eliminated. For the determination of stereosequences with a high degree of precision, synthesis of polymers with varying tacticity contents and n.m.r. experiments at higher magnetic field were of great value. While free-radical-initiated polymer obeys Bernoullian statistics, the anionically initiated polymer obtained in toluene displays first-order Markov statistics. On the other hand, anionic polymerization in THF proceeds through Bernoullian statistics.

REFERENCES

1 Farina, M. *Topics Stereochem.* 1987, **17**, 1
2 Tonelli, A. E. and Schilling, F. C. *Acc. Chem. Res.* 1981, **14**, 233
3 Randall, J. C. 'Polymer Sequence Determination', Academic Press, New York, 1977
4 Ferguson, R. C. and Ovenall, D. W. *Macromolecules* 1987, **20**, 1245
5 Tonelli, A. E. *Macromolecules* 1983, **16**, 604
6 Di Silvestro, G., Sozzani, P., Savare, B. and Farina, M. *Macromolecules* 1985, **18**, 928
7 Bovey, F. A. 'Chain Structure and Conformation of Macromolecules', Academic Press, New York, 1982
8 Harwood, H. J., Chen, T. and Lin, F. in 'NMR and Macromolecules: Sequence, Dynamics and Domain Structure' (Ed J. C. Randall), *Am. Chem. Soc. Symp. Ser.* 1984, **247**, 197
9 Bovey, F. A. and Mirau, P. *Acc. Chem. Res.* 1988, **21**, 37
10 Vogl, O. *Makromol. Chem. Macromol. Symp.* 1987, **12**, 351
11 Webster, O. W. and Sogah, D. Y. in 'Recent Advances in Mechanistic and Synthetic Aspects of Polymerization' (Eds M. Fontanille and A. Guyot), D. Reidel Publishing Co., Dodrecht, Netherlands, 1987, p. 3
12 Kalal, J. *J. Polym. Sci. Polym. Symp.* 1978, **62**, 251
13 Dhal, P. K. *PhD Thesis* IIT, Bombay, 1983
14 Fréchet, J. M. J., Bald, E. and Svec, F. *React. Polym.* 1985, **1**, 21
15 Lindsay, D. and Sherrington, D. C. *React. Polym.* 1985, **3**, 327
16 Dhal, P. K., Babu, G. N., Sudhakaran, S. and Borkar, P. S. *Makromol. Chem. Rapid. Commun.* 1985, **6**, 91
17 Dhal, P. K., Babu, G. N., Sudhakaran, S. and Borkar, P. S. *J. Polym. Sci., Polym. Chem. Edn.* 1985, **23**, 319
18 Thomson, L. F., Yau, L. and Doerrics, E. M. *J. Electrochem. Soc.* 1979, **126**, 1703
19 Dhal, P. K., Babu, G. N. and Nanda, R. K. *Macromolecules* 1984, **17**, 1131
20 Dhal, P. K. and Babu, G. N. *J. Polym. Sci., Polym. Chem. Edn.* 1984, **22**, 1817
21 Bendall, M. R., Pegg, D. T. and Doddrell, D. M. *J. Magn. Reson.* 1981, **45**, 8
22 Wulff, G., Sczepan, R. and Steigel, A. *Tetrahedron Lett.* 1986, **27**, 1991
23 Ernst, R. R., Bodenhausen, C. and Wokaun, A. 'Principles of Nuclear Magnetic Resonance in One and Two Dimensions', Oxford Science Publ., Clarendon Press, Oxford, 1987
24 Bovey, F. A. 'High Resolution NMR of Macromolecules', Academic Press, New York, 1972
25 Koening, J. L. 'Chemical Microstructures of Polymer Chains', Wiley–Interscience, New York, 1980
26 Bovey, F. A. 'Chain Structure and Conformation of Macromolecules', Academic Press, New York, 1982, p. 61