Microstructure determination of poly(1-naphthylalkyl methacrylate)s by ^{13}C n.m.r. spectroscopy

T. Radiotis
Department of Chemistry, McGill University, 801 Sherbrooke St. W., Montreal, Quebec, Canada

and A. Spyros and P. Dais*
Department of Chemistry, University of Crete, 71409 Iraklion, Crete, Greece
(Received 3 February 1992; revised 26 May 1992)

^{13}C n.m.r. spectroscopy was used to determine the microstructure of naphthalene-containing polymers obtained by free radical polymerization. The splitting of the various carbon resonances of poly(1-naphthyl methacrylate) (PNMA), poly(1-naphthylmethyl methacrylate) (PNMMA) and poly[2-(1-naphthyl)ethyl methacrylate] (PNEMA) show that these are heterotactic polymers conforming with Bernoullian statistics. Based on the calculated probability of generating a *meso* sequence at the end of the growing chain, the isotacticity appears to decrease in the sequence PNMA > PNMMA ~ PNEMA. These results are discussed in relation to the photophysical behaviour of these polymers.

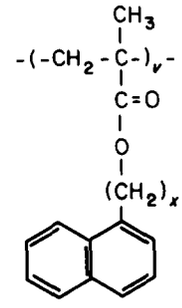
(Keywords: spectroscopy; microstructure; polymerization)

INTRODUCTION

Emission spectra and photophysical processes in polymers containing pendant aromatic groups have been investigated extensively in the last decade[1,2]. In particular, the energy transfer between pendant naphthalene chromophores can result in excimer formation, unusually efficient quenching by small molecules and energy transfer to chemically bound traps. These energy transfer processes in synthetic polymers appear to mimic similar effects in plant photosynthesis, and to have practical consequences in the photodegradation and/or photostabilization of commercial polymers.

A detailed interpretation of photophysical results requires, among other factors, a knowledge of the stereoregularity of the polymer system[3,4]. This factor determines the effective 'concentration' of the pendant chromophores on the polymer chain for efficient intrachain energy transfer.

To examine the effect of tacticity on energy migration and excimer formation, the microstructure of a series of naphthalene-containing polymers is determined here by ^{13}C n.m.r. spectroscopy. These polymer systems, poly(1-naphthyl methacrylate) (PNMA), poly(1-naphthylmethyl methacrylate) (PNMMA) and poly[2-(1-naphthyl)ethyl methacrylate] (PNEMA), constitute a series in which the naphthalene chromophore is located progressively further from the main chain. The emission characteristics of these polymers are discussed in relation to the microstructure of the polymer chain.



$x = 0$: PNMA
$x = 1$: PNMMA
$x = 2$: PNEMA

EXPERIMENTAL

Polymers PNMA, PNMMA and PNEMA were synthesized by free radical polymerization, and purified, according to the literature[5–7]. Molecular weights ($\overline{M}_w$) were determined by low angle laser scattering using a KMX chromatix instrument. The $\overline{M}_w$ values were 2.25×10^5, 8.38×10^5 and 1.45×10^5 for PNMA, PNMMA and PNEMA, respectively.

^{13}C n.m.r. noise-decoupled spectra at 60°C were obtained with a Varian XL-300 spectrometer operating at 75.4 MHz. The instrument conditions were: pulse angle 45° (15 μs); repetition time 2.0–2.5 s for sweep widths of 15 000 Hz; 10 000–15 000 transients on 32K memory were accumulated for each experiment. Sweep widths of

*To whom correspondence should be addressed

0032-3861/93/091846-04

1500–2000 Hz and repetition times of >8 s were used to achieve higher resolution for $^{13}C{=}O$ resonances. Samples were 10% w/v in 1,1,2,2,-tetrachloroethane-d_2 (TCE). Chemical shifts were measured relative to the solvent peak and converted to δ (tetramethylsilane, TMS) according to the relationship: $\delta_{TMS} = \delta_{TCE} + 75.50$ ppm. Peak intensities were determined by curve-fitting[8]. The best fit was obtained using Lorentzian-shaped lines and a broad third-order baseline.

RESULTS

Figure 1 shows the ^{13}C n.m.r. spectrum of PNEMA. Peak assignment of the backbone and methyl carbon resonances was made by analogy with the ^{13}C spectra of poly(methyl methacrylate) (PMMA)[9], and confirmed by correlation with C–H multiplets in the off-resonance spectra. The side chain methylene carbons were assigned by simply comparing the spectrum in *Figure 1* with those of PNMMA and PNMA (not shown), since the side chain of these polymers increases in length by one methylene unit in going from PNMA to PNEMA. The carbonyl resonances were safely assigned as those appearing at the lowest fields. The naphthyl carbons were assigned on the basis of model compounds[10], i.e. 1-acetoxy,1-hydroxymethyl and 1-carbomethoxy naphthalenes and verified, where possible, by T_1 measurements. These assignments are summarized in *Table 1*.

Figure 1 shows that several carbons in PNEMA are stereosensitive. However, the degree of stereosensitivity as reflected in these carbons differs within the polymer series. The highest resolution is offered by PNEMA, whereas the poorest is observed for PNMA, with PNMMA being intermediate (*Figure 2*). The carbonyl peak of PNEMA is resolved into eight pentads. The different peaks are shown in an expanded form in *Figure 1* and their assignment is based on the probability, P_m, obtained from the triad analysis, and the assumption that PNEMA fits Bernoullian statistics.

Table 2 shows that there is very good agreement between calculated and measured intensities. The resonance of the tertiary backbone carbon and that of the methyl carbon split into triad tacticity (*Figure 1*). Further splitting into pentads is incomplete at the resolution used. Although the resolution for these peaks is not as good as for the $^{13}C{=}O$ resonance, the triad tacticities estimated from these peak intensities agree closely with those obtained from $^{13}C{=}O$ (*Table 2*).

Among the peaks of PNMMA which are stereosensitive, the $^{13}C{=}O$ resonance shows the highest resolution (*Figure 2*). Six pentads are resolved in total fitting Bernoullian statistics with $P_m = 0.252$, as shown in *Table 2*. The splitting pattern of the remaining resonances of PNMMA (*Figure 2*) is similar to that of PNEMA. Integrated intensities for these resonances are summarized in *Table 2*.

The splitting of the $^{13}C{=}O$ resonance in PNMA is very poor to allow statistical analysis, whereas the splitting of the $^{13}CH_3$ resonance (*Figure 2*) is not adequate for assignment beyond triad tacticity (*Table 2*).

The splitting of the methylene signals for the polymers in the series can be tentatively assigned to mixed dyad and tetrad stereosequences, analogous to what has been suggested by several authors for PMMA[9]. In the present

Table 1 ^{13}C chemical shifts[a] for PNMA, PNMMA and PNEMA in TCE-d_2

Carbons	PNMA	PNMMA	PNEMA
C=O	177.70–175.50[b]	180.30–176.10	180.30–176.70
CH_3	24.90–19.50	24.30–17.30	23.40–17.60
–C–	48.27	48.00–45.70	48.30–45.60
CH_2	58.00–51.90	58.50–51.50	58.50–51.70
O–$\underline{C}H_2$	–	66.19	–
O–$\underline{C}H_2$–CH_2	–	–	66.51
O–$\underline{C}H_2$–$\underline{C}H_2$	–	–	33.22
C-1[c]	148.70–146.50	132.70–132.44	135.18–135.02
C–2	118.57	128.75	128.49
C–3	126.75	126.81	127.10
C–4	127.67	130.17	129.10
C–5	129.45	130.55	130.38
C–6	128.18	127.51	127.22
C–7	127.97	128.11	127.80
C–8	122.39	124.95	125.08
C–4a	136.04	135.07	135.34
C–8a	–[d]	133.06	133.51

[a] In ppm relative to TMS. Solutions of 10% w/v
[b] Range of chemical shifts due to microtacticity
[c] Naphthyl carbons
[d] Peak at ~129 ppm, not resolved

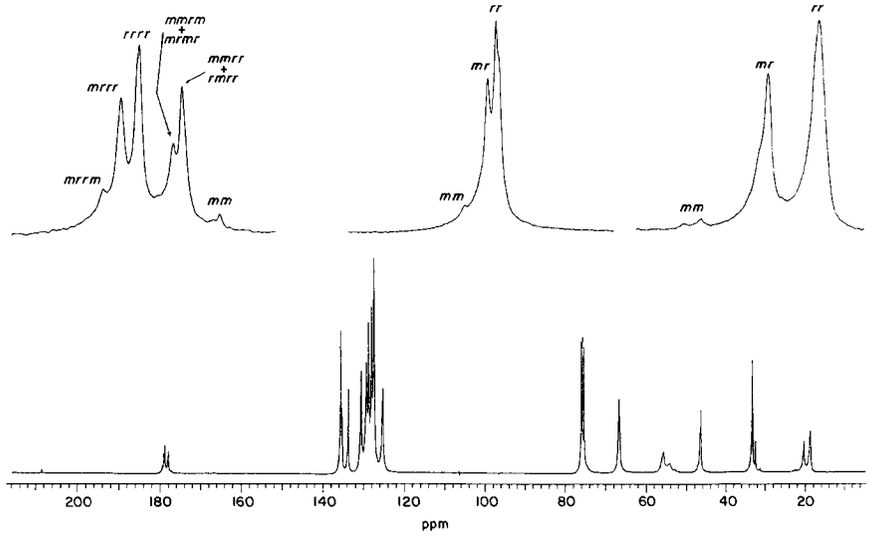


Figure 1 ^{13}C n.m.r. spectrum and expanded spectra of various stereosensitive carbon resonances of PNEMA in TCE-d_2 at 60°C

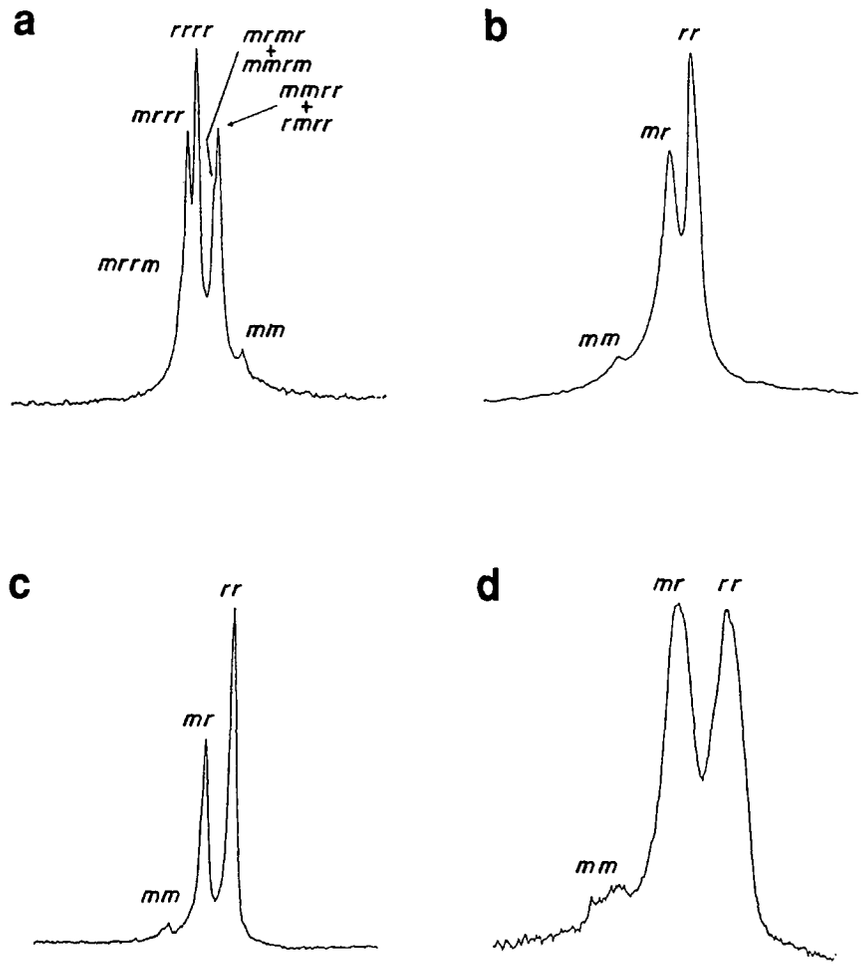


Figure 2 ^{13}C n.m.r. expanded spectra of various stereosensitive carbon resonances: (a) $^{13}C{=}O$ PNMMA; (b) t-^{13}C PNMMA; (c) $^{13}CH_3$ PNMMA; (d) $^{13}CH_3$ PNMA

Table 2 Experimental and calculated microtacticity[a] for PNMA, PNMMA and PNEMA

	PNEMA						PNMMA						PNMA	
	C=O		t-C		CH_3		C=O		t-C		CH_3		CH_3	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
(*mm*)	0.06	0.07	0.08	0.07	0.07	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.10	0.10
(*mr*)	0.38	0.38	0.40	0.38	0.38	0.38	0.37	0.38	0.39	0.38	0.38	0.38	0.42	0.42
(*rr*)	0.56	0.55	0.52	0.55	0.55	0.55	0.57	0.56	0.55	0.56	0.56	0.56	0.48	0.48
(*mmmm*) (*mmmr*) (*rmmr*)	0.06	0.07					0.06	0.06						
(*mmrm*) (*mrmr*)	0.10	0.10					0.10	0.10						
(*mmrr*) (*rmmr*)	0.28	0.28					0.27	0.28						
(*rrrr*)	0.30	0.30					0.32	0.31						
(*mrrr*)	0.22	0.21					0.22	0.21						
(*mrrm*)	0.04	0.04					0.03	0.04						
P_m			0.260						0.252				0.309	

[a] Assuming Bernoullian statistics

case, however, the individual components are not resolved well enough (*Figure 1*) to allow any significant attribution.

DISCUSSION

Stereochemical features of the polymers described here, as determined from their ^{13}C n.m.r. spectra, indicate that these polymer systems are heterotactic, fitting Bernoullian statistics. Based on the calculated probability of *meso* addition, P_m, the isotacticity appears to decrease in the sequence PNMA > PNMMA ~ PNEMA, following the same order of excimer formation observed[5–7,11,12] for these polymers under identical conditions. The observed decrease in the monomer emission intensity with decreasing side chain length, suggests that the higher isotacticity in the shorter side chain promotes through-space and/or through-bond interactions between an excited and a ground state naphthalene chromophore, leading to acceleration of the non-radiative decay of the former. The combination of rapid excimer formation and photoreactivity[11] of PNMA results in an inefficient energy transfer in 9-vinylanthracene-terminated PNMA[11]. Nevertheless, energy transfer is almost equally efficient in copolymers of NEMA and NMMA with 9-anthrylmethyl methacrylate, and/or between PNEMA and PNMMA polymers containing terminal anthracene traps[6,12].

ACKNOWLEDGEMENTS

Financial assistance from the University of Crete is gratefully acknowledged. This work was also supported by NATO Grant CRG910406.

REFERENCES

1 Holden, D. A. and Guillet, J. E. 'Development in Polymer Photochemistry', Applied Science, Barking, 1980
2 Semerak, S. N. and Frank, C. W. *Adv. Polym. Sci.* 1983, **54**, 33
3 Houben, J. L., Natucci, B., Solaro, R., Collela, O., Chiellini, E. and Ledwith, A. *Polymer* 1978, **19**, 811
4 Ishiie, T., Matsunaga, S. and Handa, T. *Makromol. Chem.* 1976, **177**, 283
5 Aspler, J. S. and Guillet, J. E. *Macromolecules* 1979, **12**, 1082
6 Holden, D. A. and Guillet, J. E. *Macromolecules* 1980, **13**, 289
7 Holden, D. A., Rendal, W. A. and Guillet, J. E. *Ann NY Acad. Sci.* 1981, **366**, 11
8 Bosse, F. *MSc. Thesis* McGill University, 1990
9 Randall, J. C. 'Polymer Sequence Determination, Carbon-13 Method', Academic Press, New York, 1977
10 Hansen, P. E. *Org. Magn. Reson.* 1979, **12**, 109
11 Merle-Aubry, L., Holden, D. A., Merle, Y. and Guillet, J. E. *Macromolecules* 1980, **13**, 1138
12 Holden, D. A., Wang, P. Y. K. and Guillet, J. E. *Macromolecules* 1980, **13**, 295