Eur. Polym. J. Vol. 19, No. 5, pp. 433–438, 1983
Printed in Great Britain. All rights reserved

0014-3057/83/050433-06$03.00/0

SYNTHESIS, STEREOCHEMISTRY AND FLUORESCENCE PROPERTIES OF POLYSTYRENES HAVING CARBAZOLE SUBSTITUENTS

R. Solaro[1], G. Galli[1], F. Masi[1], A. Ledwith[2] and E. Chiellini[1,3]

[1]Istituto Chimica Organica Industriale, Università di Pisa, Centro CNR Macromolecole Stereordinate Otticamente Attive, Via Risorgimento 35, 56100 Pisa, Italy,
[2]Donnan Laboratories, IPI Chemistry Department, The University of Liverpool, Liverpool L69 3BX, U.K. and
[3]Istituto Chimica Generale, Facoltà di Ingegneria, Università di Pisa, Via Diotisalvi 2, 56100 Pisa, Italy

(*Received* 14 *September* 1982)

Abstract—Poly(styrene)s bearing carbazole substituents at various positions were synthesised by homopolymerisation of 3-(9-carbazolylmethyl)styrene and 4-(9-carbazolylmethyl)styrene and by chemical modification of preformed poly(styrene)s prepared in the presence of different initiators. Main chain stereochemistry of the polymer samples was investigated by ^{13}C-NMR and related to the initiation process. The fluorescence emission spectra were independent of the stereochemistry of polymer backbone and exhibited only monomer emission. In no case was there any evidence of excimer fluorescence. In contrast, energy migration appeared to be very efficient, as evaluated by measurements of the degree of fluorescence polarisation relative to that of a structurally related model compound

INTRODUCTION

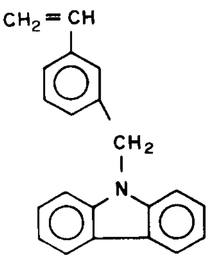
Studies of the fluorescence of polymers having aromatic substituents have been of considerable value in understanding the nature and efficiency of conformational changes in polymer backbone structures [1]. In particular, the relative ease of formation of excimers, as evidenced by the ratio of monomer to excimer emission, provides a measure of either the freedom with which a polymer chain with aromatic substituents may rotate to allow eclipsed arrangements of the aromatic groups, or the propensity of the particular aromatic chromophores to form stable excimers.

Poly(*N*-vinylcarbazole) has been of special interest because of the possible inter-relation of its fluorescence properties with applications as a photoconductor [2]. Arising from the important photoconductivity characteristics of poly(*N*-vinylcarbazole), there have been many reports of the synthesis and properties of polymers having carbazole substituents [3–8], in addition to studies of polymers of vinylcarbazoles in which the heteroaromatic unit is attached directly to the polymer backbone via the various ring positions [9–14]. A conclusion which may be drawn from all the previous reports is that excimer emission is evident only for polymers in which the carbazole group is attached directly to the polymer backbone [6, 13]. Normally copolymers of *N*-vinylcarbazole do not show excimer emission except when the copolymer composition is such as to allow for relatively long sequences of carbazole units [15–17]. One possible exception to the general rule is that copolymers of *N*-vinylcarbazole with fumaric derivatives, thought to have an alternating structure, exhibit a long wavelength emission typical of excimer formation [18].

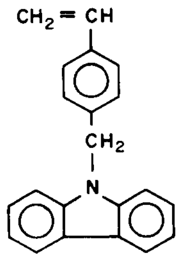
It is pertinent that even for poly(*N*-vinylcarbazole), the main chain stereoregularity is not fully established and it remains to be proven whether high degrees of tacticity in poly(*N*-vinylcarbazole) will enhance or diminish excimer population [11, 15].

Carbazole-substituted styrenes **1** and **2** may be synthesised from the commercially available mixture of *meta*- and *para*chloromethyl styrenes and would be anticipated to polymerise via a variety of mechanisms including stereospecific Ziegler–Natta type polymerisation.

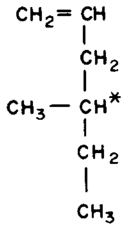
It was of interest therefore to determine the fluorescence properties of homopolymers of **1** and **2**



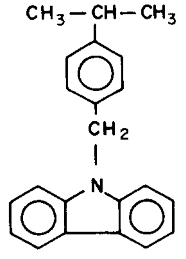
1



2



3



5

obtained by different polymerisation processes in the hope of correlating excimer emission with the main chain stereoregularity. Although it is clear that homopolymers of **1** and **2** will have the carbazole substituents remote from the polymer backbone, the relative rigidity of styrene units in the polymer might be expected to facilitate the nearest-neighbour overlap usually invoked to explain excimer formation. In the event it was observed (*loc. cit.*) that **1** and **2** could not be polymerised by the usual Ziegler–Natta catalytic process and hence it was necessary to synthesise the corresponding isotactic poly(**2**) by chemical modification of preformed isotactic poly(styrene).

The present paper gives full details of the synthesis and fluorescence properties of poly(styrene)s having *meta-* and *para*carbazole substituents.

EXPERIMENTAL

Materials

Monomers. 3-(9-carbazolylmethyl)styrene (**1**) and 4-(9-carbazolylmethyl)styrene (**2**) were synthesised according to the procedure of Gibson and Bailey [4]. (S)-4-methyl-1-hexene (**3**) $[\alpha]^{25}_{D}$ − 2.82 (neat), optical purity 93.5% [19] was prepared as previously reported [20]. Commercially available styrene (**4**) was purified according to the conventional procedure and distilled *in vacuo* immediately before use. 2-[4-(9-carbazolylmethyl)phenyl]propane (**5**) was synthesised as previously reported [8].

Polymers. **1** and **2** were polymerised by free radical and Ziegler–Natta catalysts as reported in Table. 1. Copolymerisations of **1** and **2** with **3** were carried out in toluene in the presence of a Ziegler–Natta catalyst (Table 2). The polymeric products were isolated by precipitation into methanol and purified by dissolution in dichloromethane and reprecipitated in acetone. The crude reaction products were then fractionated with *n*-pentane at room temperature. Styrene was polymerised with free radical, cationic and Ziegler–Natta initiators as reported in Table 3. All the polymers were purified by multiple precipitations from chloroform into methanol. The Ziegler–Natta poly(styrene) was fractionated with boiling methanol, acetone and toluene in that order.

Poly(styrene)s were reacted with CH_3OCH_2Cl in the presence of $ZnCl_2$ at room temperature for 50 hr (Run ZN2 at 30°C for 120 hr) yielding 100% chloromethylated products [21]. Subsequent transformation with carbazole was performed under phase-transfer conditions in the presence of tetra-*n*-butylammonium bromide (TBAB) at 60°C for 5 hr, giving complete carbazolylmethyl substitution [8] (Table 4).

Polymer characterisations

Viscosity measurements were performed with a dilution viscometer in toluene at 30°C. Molecular weights ($\bar{M}_v$)

Table 1. Polymerisation of 3-(9-carbazolylmethyl)styrene (**1**) and of 4-(9-carbazolylmethyl)styrene (**2**) under various conditions

	Polymerisation conditions*				Polymeric product	
Run	Monomer	Catalyst	Mon/Cat (mol/mol)	Conversion (%)	M_n† ($\cdot 10^{-3}$)	*p*‡
H1	**1**	AIBN§	100	85.4	21.9	−0.002
H2		$Al(iBu)_3/TiCl_4$‖	30	67.4	37.9	−0.007
H3	**2**	AIBN§	100	79.3	18.6	−0.006
H4		$Al(iBu)_3/TiCl_4$‖	30	56.2	50.8	0.004

* At 70°C for 120 hr.
† By membrane osmometry, in chlorobenzene.
‡ Degree of polarisation (see Experimental).
§ In benzene.
‖ In toluene; Al/Ti = 3.5 (mol/mol).

Table 2. Copolymerisation of 3-(9-carbazolylmethyl)styrene (**1**) and of 4-(9-carbazolymethyl)-styrene (**2**) with (S)-4-methyl-1-hexene (**3**)

	Polymerisation conditions*					Polymeric product‡	
	Carbazolyl(styrene)						
Run	type	mmol	%mol	Duration (hr)	Conv.† (%)	Amount of **3**§ (%mol)	$[\alpha]^{25}_{D}$‖
C-13	**1**	1.8	33.3	79	9	43.8	−51.2
C-23	**2**	2.5	33.3	65	7	11.5	−10.6

* In toluene at 70°C in the presence of $Al(iBu)_3/TiCl_4$; comonomer concentration 0.6 M; comonomers/Ti molar ratio = 30; Al/Ti = 3.5.
† Evaluated as (weight of precipitated polymer/weight of starting monomers) × 100.
‡ Mixture of homopolymers, as proved by extraction with solvents.
§ ^1H-NMR spectroscopy.
‖ In chloroform.

Table 3. Polymerisation of styrene (**4**) under various catalytic conditions

Run	Catalyst	Mon/Cat (mol/mol)	Solvent	Temp. (°C)	Time (hr)	Conversion (%)	$\overline{M}_v$* ($\cdot 10^{-3}$)
R	AIBN	100	benzene	70	24	78.9	12
C	$EtAlCl_2$	150	toluene	−78	24	76.7	6
Z–N	$Al(iBu)_3/TiCl_3$†	15	*n*-heptane	45	48	31.7‡	170‡

* By viscometry: $[\eta] = 1.1 \cdot 10^{-4}\,\overline{M}_v^{0.725}$ in toluene at 30°C.
† In the presence of $Zn(iBu)_2$; Al/Ti = 2.5 and Al/Zn = 2.0 (mol/mol).
‡ Toluene soluble fraction.

were evaluated from the equation $[\eta] = 1.1 \cdot 10^{-4}\,\overline{M}_v^{0.725}$ (in toluene, at 30°C) [22] for poly(styrene) samples. Number-average molecular weights ($\overline{M}_n$) were determined by means of a Hewlett–Packard membrane osmometer in chlorobenzene solution.

I.R. spectra were recorded on a Perkin–Elmer 283B spectrophotometer on polymer films cast from solution or on KBr discs. U.V. spectra were taken with a Cary 14 Spectrophotometer in CH_2Cl_2 solution in the 330–230 nm spectral region (path length 0.1–1 cm). Fluorescence emission and excitation spectra were taken by a Perkin–Elmer MPF43 Spectrofluorimeter on outgassed polymer solutions (10^{-5} M carbazole units concentration) both in CH_2Cl_2 and 2-methyltetrahydrofuran (2Me-THF) at room temperature. The spectra were not corrected for the wavelength dependence of the detector response. Quenching experiments were performed on aerated polymer solutions ($5 \cdot 10^{-5}$ M carbazole units concentration) in CH_2Cl_2 containing maleic anhydride (0–0.05 M).

Fluorescence polarisation measurements were performed in 2Me-THF glassy solution at 77°K at the excitation and emission wavelengths of 330 and 350 nm respectively. The degree of polarisation *p* was evaluated from the relation [23]:

$$p = \frac{I_{\parallel} - GI_{\perp}}{I_{\parallel} + GI_{\perp}}$$

where $I_{\parallel}$ and $I_{\perp}$ are the components of emitted radiation parallel and perpendicular to the plane of polarised excitation and $G = I_{\perp}/I_{\parallel}$ is a correction factor due to instrumental anisotropy. The ^{1}H-NMR spectra were recorded on a Varian T-60 Spectrometer in $CDCl_3$ using TMS as an internal standard. The ^{13}C-NMR spectra were recorded at 25.2 MHz by a Varian XL100 Spectrometer on polymer solutions in $CDCl_3$ with TMS as internal standard. The spectra were ^{1}H-noise decoupled and obtained after accumulation of 10–80 thousand transients.

RESULTS AND DISCUSSION

Synthesis and characterisation

As reported by Gibson and Bailey [3, 4] it was observed that **1** and **2** readily polymerise under the influence of a typical radical initiator (Table 1). By using a Ziegler–Natta catalyst, fairly high yields were obtained in the homopolymerisations of **1** and **2**, whereas very low conversions were observed in copolymerisations with (S)-4-methyl-1-hexene (**3**) (Tables 1 and 2). Moreover, the copolymerisation products can be easily separated by solvent extraction into two fractions, one soluble in *n*-pentane consisting mainly of poly[(S)-4-methyl-1-hexene], and an insoluble part containing the homopolymer of the corresponding styrene derivative. Similarly, a mixture of two homopolymers was obtained in copolymerisation runs of *N*-vinylcarbazole with **3** in the presence of a typical Ziegler–Natta catalyst [24]. These results suggest that the anionic coordinate mechanism, capable of giving highly isotactic polymers, is apparently not operating in the polymerisation of carbazole-containing monomers. In order to obtain polymeric products, having known main chain stereochemistry, it was therefore necessary to adopt an indirect synthetic method.

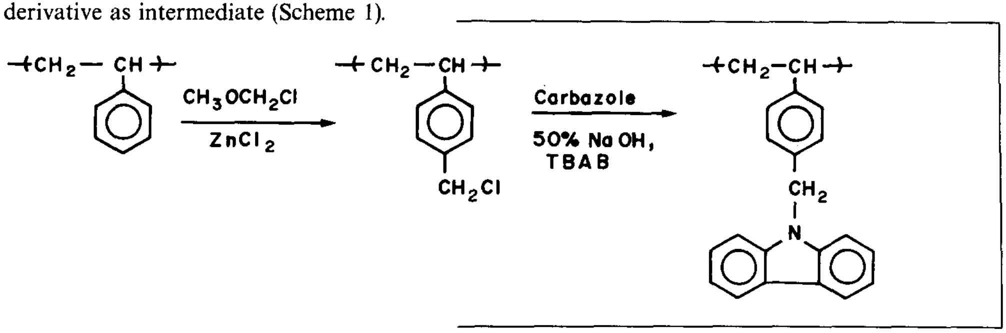
Poly(styrene)s prepared in the presence of various catalytic systems (Table 3) and having well established and different types and degrees of tacticity were selec-

Table 4. Synthesis and characteristics of poly[4-(9-carbazolylmethyl)styrene] [poly(**2**)] obtained by chemical modification

	Starting poly(styrene)		Reaction product					
			Chloromethylation*			Carbazolylation†		
Run	Catalyst	$\overline{M}_v$‡ ($\cdot 10^{-3}$)	Yield (%)	$CHCl_3$ extract (%wt)	Substitution§ degree (%)	Yield (%)	$\overline{M}_n$‖ ($\cdot 10^{-3}$)	*p*¶
R1	AIBN	12	83.6	100	100	72.8	41.3	0.008
C1	$AlEtCl_2$	6	65.2	100	100	54.7	9.3	0.032
Z–N1	$Al(iBu)_3/TiCl_3$	170	81.1	37	50	62.3		−0.005
Z–N2	$Al(iBu)_3/TiCl_3$	170	85.8**	28	100	50.3	38.3	−0.006

* In CH_3OCH_2Cl solution in the presence of $ZnCl_2$ at room temperature for 50 hr.
† Under phase-transfer conditions (TBAB, 50% NaOH) at 60°C for 5 hr; 100% degree of substitution.
‡ In toluene at 30°C.
§ By ^{1}H-NMR in $CDCl_3$.
‖ By membrane osmometry in chlorobenzene.
¶ Degree of polarisation (see Experimental).
** At 30°C for 120 hr.

tively substituted in the *para*-position by the 9-(carbazolylmethyl) group, via the corresponding chloromethylated derivative as intermediate (Scheme 1).



It was thus possible to obtain products with up to 100% ring substitution (Table 4). We have to observe however that about 70% of the product obtained in the chloromethylation of the Ziegler–Natta poly(styrene) was insoluble in most common organic solvents. The subsequent modifications and characterisations were therefore performed only on the soluble fraction.

The polymeric products prepared by both homopolymerisation and chemical transformation were characterised by i.r., u.v. and NMR spectroscopy and shown to have the expected regular head-to-tail structure typical of vinyl polymers. In Fig. 1 the i.r. spectra of poly(**1**) and poly(**2**) are represented and, contrary to other reports [3], they show typical absorption bands of the aromatic moieties.

As previously reported [8], the u.v. and ^{1}H-NMR spectra do not exhibit any characteristic band attributable to the occurrence of carbazole-carbazole interactions [16].

^{13}C-*NMR spectra*

In order to gain more information on the main chain tacticity, homopolymers prepared by different routes were investigated by ^{13}C-NMR spectroscopy. Figure 2 shows the ^{13}C-NMR spectra of model compound **5** and of free radically prepared poly(**1**) and poly(**2**), as typical examples. It is interesting to note that the signals present at about 45 and 145 ppm, attributable respectively to main chain carbon atoms (C-α and C-β) and to the benzene quaternary carbon atom linked to the polymer backbone (C-1), are structured and show appreciable differences in samples prepared by different routes. Due to overlap, the broad signals of the C-α and C-β are of little diagnostic value, whereas the C-1 signal is rather well resolved and can be in principle related to main chain stereochemistry.

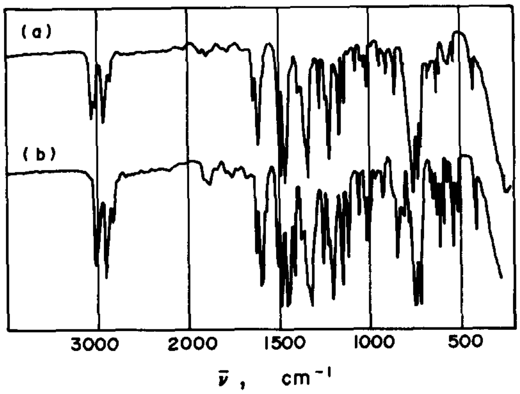


Fig. 1. I.R. spectra of (*a*) poly(**1**) and (*b*) poly(**2**) prepared by radical initiation.

In order to obtain such a correlation, the C-1 signals of poly(**2**) prepared from poly(styrene) by a sequence of reactions believed not to affect the polymer stereochemistry [25] (Scheme 1) were compared with those of the parent poly(styrene)s (Fig. 3). Even if in the literature there is not complete agreement on the assignment of the splittings of the C-1 signal

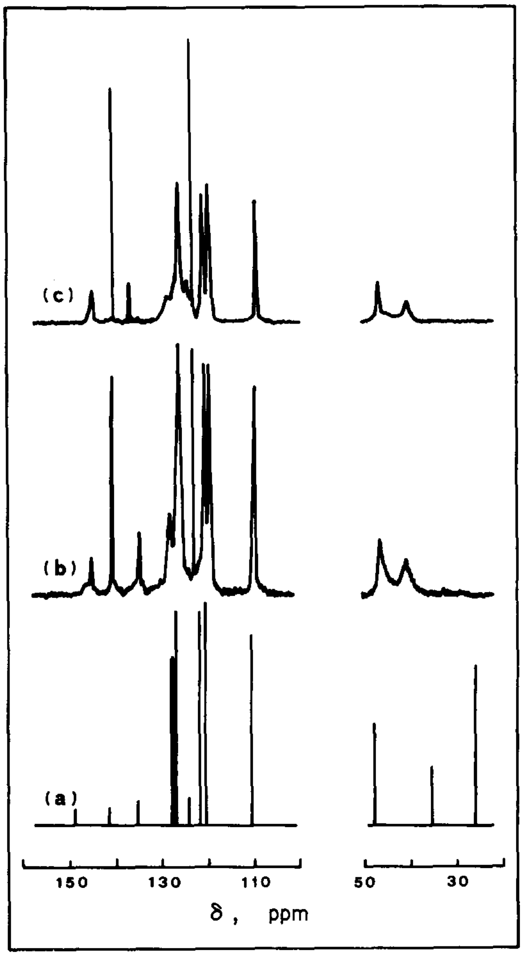


Fig. 2. ^{13}C-NMR spectra of: (*a*) 2-[4-(9-carbazolylmethyl)-phenyl]propane, (*b*) poly(**2**) and (*c*) poly(**1**) prepared in the presence of AIBN.

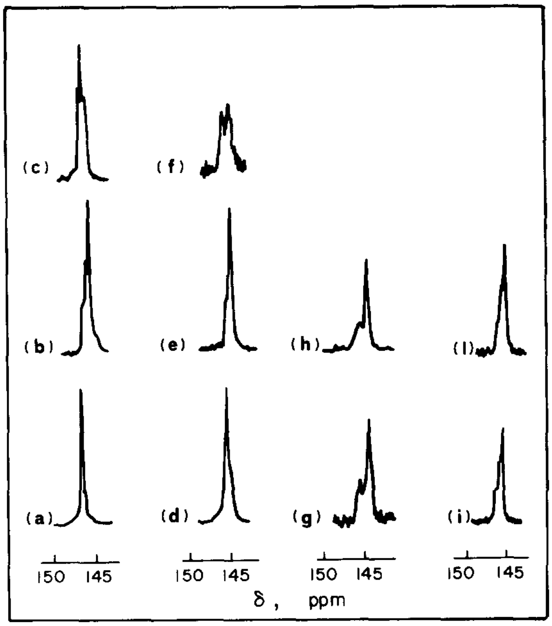


Fig. 3. ^{13}C-NMR spectra of C-1 signal of: (*a–c*) poly(styrene) samples Z-N, R and C; (*d–h*) poly(**2**) samples Z-N-2, R1, C1, H4 and H3; (*i,l*) poly(**1**) samples H2 and H1.

[26–31], it is well established that poly(styrene) prepared in the presence of radical, cationic and Ziegler–Natta initiators contains about 70, 50 and 10% of *racemic* dyads respectively [26].

The C-1 signal of poly(**2**) is split into two components centred at 144.0 and 145.0 ppm, here attributed to *racemic* and *meso* dyads, since their intensity closely corresponds, in samples prepared by chemical modification, to *racemic* and *meso* dyad content of the parent poly(styrene) (Table 5).

A slight decrease of the degree of isotacticity is observed in the polymer sample obtained by transformation of the Ziegler–Natta poly(styrene) (Run Z–N2), probably due to fractionation occurring in the chloromethylation reaction and subsequent isolation of the soluble product.

Table 5. Dyad tacticity of poly(styrene) and poly(styrene)s containing carbazole substituents prepared by different routes

Run	Polymer Type	 Catalyst	r dyads* (%)
H1	Poly(**1**)	AIBN	72
H2		Z-N†	72
H3		AIBN	75
H4		Z-N†	71
R1	Poly(**2**)	AIBN	75
C-1		$BF_3 \cdot 0Et_2$	54
ZN-2		Z-N†	20
R	Poly(styrene)	AIBN	72
C		$BF_3 \cdot 0Et_2$	52
Z-N		Z-N†	10

* Evaluated from the C-1 signal in the ^{13}C-NMR spectrum.

† Ziegler–Natta initiator (see Tables 1, 3 and 4).

The C-1 signal of poly(**1**) is split into three components centred at 144.0, 144.6 and 145.0 ppm. In this case no correlation with polymeric precursors can be made and the relative intensities of the three peaks, that could be tentatively assigned to *syndio*, *hetero* and *isotactic* triads respectively, do not satisfy a Bernoullian statistics. It is therefore very likely that, as in the case of poly(styrene), the C-1 splittings arise from higher order stereo-sequences, and the similarity of the C-1 resonances of radical poly(styrene) and poly(**1**) allows a tentative evaluation of the dyad tacticity of poly(**1**) by assigning the higher field signal to rrrr pentads as in poly(styrene) [31] (Table 5).

Significantly, the homopolymerisations of **1** and **2** with a typical Ziegler–Natta catalyst yielded polymeric products having main chain tacticity similar to the polymer obtained by free radical initiation. These results, in full agreement with the copolymerisation data, further indicate that the anionic coordinate mechanism is not effective in the presence of carbazole derivatives and that, at least under the adopted experimental conditions, the Ziegler–Natta catalyst behaves very much as a free radical initiator [32].

Fluorescence emission spectra

Figure 4 shows that the fluorescence spectra of poly(**2**), made either by homopolymerisation or chemical modification of poly(styrene)s, show mainly the usual structured isolated carbazole emission bands at 350 and 370 nm in both CH_2Cl_2 and 2Me-THF solvents. In this respect the fluorescence of poly(**2**) [and poly(**1**)] is identical with that of the model compound **5**. However, in CH_2Cl_2 solvent (but not in 2Me-THF) poly(**2**) exhibits enhanced fine structure at wavelengths >390 nm. It is noteworthy that the enhanced long wavelength emission is not observed in the fluorescence spectra of poly(**1**) and that it does not appear to arise via the usual excimer-like

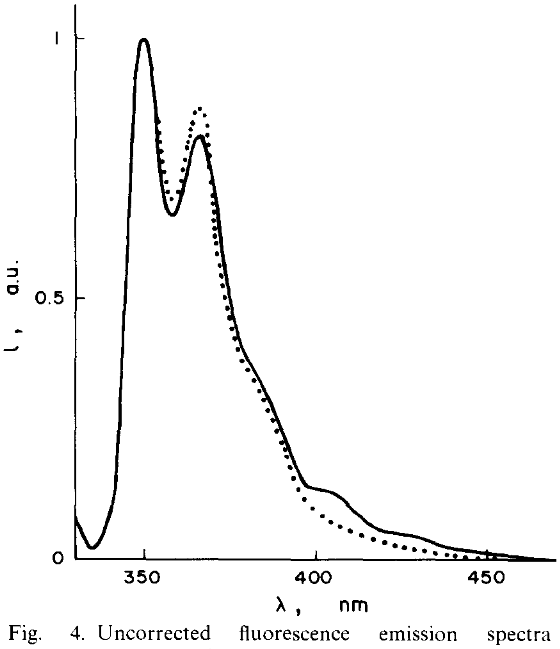


Fig. 4. Uncorrected fluorescence emission spectra (exc. = 330 nm) in chloroform solution of: (——) poly(**2**); (····) poly(**1**) and **5**.

interactions. In fact, the intensities of the bands at about 408 and 430 nm relative to the intensity of the band at 350 nm are not significantly affected in quenching experiments in the presence of both oxygen and maleic anhydride [15]. Furthermore, the excitation spectra observed at 350 and 408 nm are identical and consistent with the existence of only one emitting species. However, energy migration in all types of carbazole-containing polymers appears to be very efficient, as shown by the very substantial degrees of depolarisation noted, in the present work (Table 1), for poly(**1**) and poly(**2**) in contrast to that of the model compound **5** ($p = 0.156$). For the polymers obtained by chemical modification of poly(styrene), depolarisation is important for all the samples (Table 4), however we should note that depolarisation is least for the sample obtained from cationically prepared (mainly atactic and fairly low molecular weight) poly(styrene). Even allowing for the imprecision of depolarisation data, the difference is significant.

It is remarkable that a very high degree of fluorescence polarisation is observed even for the sample containing only 50% of carbazole substituents (Run ZN1 in Table 4), thus suggesting that exciton migration can occur also between carbazole chromophores separated by a small number of styrene units. As a consequence the lack of excimer emission in the investigated samples must be attributed to the absence of excimer-forming sites that should be otherwise populated rather efficiently by exciton migration.

These data lend further support to earlier observations that, in contrast to many other types of polymers with aromatic chromophores, polymers containing carbazole groups do not exhibit typical excimer emissions unless the carbazole group is attached directly to the polymer backbone [6, 13].

CONCLUSIONS

Carbazole-containing styrenes **1** and **2** can easily polymerise both by free radical and Ziegler–Natta initiators. However, in the latter case the usual anionic coordinate mechanism is not effective. In fact, homopolymers obtained in the presence of both AIBN and $Al(iBu)_3/TiCl_4$ are characterised by the same main chain tacticity, as evidenced by ^{13}C-NMR. Correspondingly attempted copolymerisation of **1** and **2** with (S)-4-methyl-1-hexene (**3**) gave only mixtures of homopolymers. On the contrary, samples of poly(**2**) having prevailing syndiotactic, atactic and isotactic structures can be successfully prepared by chemical modification of suitable preformed poly(styrene)s. Fluorescence emission spectra of the samples under investigation are independent of monomer chemical structure and polymer backbone tacticity and exhibit only the emission typical of an isolated carbazole chromophore. No excimer emission is detectable. In all cases energy migration appears to be very efficient and it is concluded that the absence of excimer fluorescence implies a very low concentration of excimer-forming sites. This conclusion is supported by u.v. and ^1H-NMR spectra of poly(**1**) and poly(**2**) which indicate the absence of bands attributable to the onset of carbazole–carbazole interactions.

These results further substantiate previous observations that carbazole-containing polymers exhibit excimer fluorescence only when the carbazole moiety is directly linked to the polymer backbone.

Acknowledgement—The authors are grateful to S.R.C. (U.K.) for granting a Visiting Fellowship to G.G.

REFERENCES

1. D. A. Holden and J. E. Guillet, *Developments in Polymer Photochemistry*, (Edited by N. S. Allen), Vol. I, p. 27. Applied Science, London (1980).
2. R. C. Penwell, B. N. Ganguly and T. W. Smith, *J. Polym. Sci., Macromol. Rev.* **13,** 63 (1978).
3. H. W. Gibson and F. C. Bailey, *Macromolecules* **9,** 688 (1976).
4. H. W. Gibson and F. C. Bailey, *Macromolecules* **10,** 602 (1977).
5. M. Keyanpour-Rad, A. Ledwith, A. Hallam, A. M. North, M. Breton, C. Hoyle and J. E. Guillet, *Macromolecules* **11,** 1114 (1978).
6. A. Ledwith, N. J. Rowley and S. M. Walker, *Polymer* **22,** 435 (1981).
7. H. Nomori, T. Enomoto, M. Yoshikawa and M. Hatano, *Makromolek. Chem.* **177,** 3077 (1976).
8. E. Chiellini, R. Solaro, F. Ciardelli, G. Galli and A. Ledwith, *Polym. Bull.* **2,** 577 (1980).
9. W. Klöpffer, *J. chem. Phys.* **50,** 2337 (1969).
10. G. E. Johnson, *J. chem. Phys.* **62,** 4697 (1975).
11. A. Itaya, K. Okamoto and S. Kusabayashi, *Bull. chem. Soc. Japan* **49,** 2082 (1976).
12. K. P. Ghiggino, R. D. Wright and D. Phillips, *Eur. Polym. J.* **14,** 567 (1978).
13. M. Keyanpour-Rad, A. Ledwith and G. E. Johnson, *Macromolecules* **13,** 222 (1980).
14. E. Chiellini, R. Solaro and A. Ledwith, *Makromolek. Chem.* **179,** 1929 (1978).
15. J. L. Houben, B. Natucci, R. Solaro, O. Colella, E. Chiellini and A. Ledwith, *Polymer* **19,** 811 (1978).
16. E. Chiellini, R. Solaro, A. Ledwith and G. Galli, *Eur. Polym. J.* **16,** 875 (1980).
17. E. Chiellini, R. Solaro, G. Galli and A. Ledwith, *Macromolecules* **13,** 1654 (1980).
18. G. Galli, R. Solaro, E. Chiellini and A. Ledwith, *Polymer* **22,** 1088 (1981); P. F. Skilton, R. Sakurovs and K. P. Ghiggino, *Polym. Photochem.* **2,** 409 (1982).
19. P. Pino and L. Lardicci, *Chem. Ind., Lond.* 483 (1959).
20. P. Pino, L. Lardicci and L. Centoni, *Gazz. Chim. Ital.* **91,** 428 (1961).
21. A. D. Jones, *Ind. Engng Chem.* **44,** 2686 (1952).
22. F. Danusso and G. Moraglio, *J. Polym. Sci.* **24,** 161 (1957).
23. T. Azumi and S. P. McGlynn, *J. chem. Phys.* **37,** 2413 (1962).
24. E. Chiellini, R. Solaro, M. Palmieri and A. Ledwith, *Polymer* **17,** 641 (1976).
25. E. Chiellini and C. Carlini, *Makromolek. Chem.* **178,** 2545 (1977).
26. K. Matsuzaki, T. Uryu, K. Osada and T. Kawamura, *Macromolecules* **5,** 816 (1972).
27. U-D. Standt and J. Klein, *Makromolek. Chem., Rapid Commun.* **2,** 41 (1981).
28. L. F. Johnson, F. Heatley and F. A. Bovey, *Macromolecules* **3,** 175 (1970).
29. Y. Inoue, A. Nishioka and R. Chujo, *Makromolek. Chem.* **156,** 207 (1972).
30. J. Randall, *J. Polym. Sci., Polym. Phys. Ed.* **13,** 889 (1975).
31. S. Suparno, J. Lacoste, S. Raynal, J. F. Regnier, F. Schue, R. Sempere and J. Sledz, *Polym. J.* **12,** 861 (1980).
32. E. Chiellini and R. Nocci, *J. Polym. Sci., Polym. Chem. Ed.* **11,** 493 (1973).