Chiroptical and fluorescence properties of copolymers of (−)menthyl acrylate and (−) menthyl methacrylate with 1-vinylnaphthalene

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Copolymerization of (−)menthyl acrylate(MtA) and (−)menthyl methacrylate(MtMA) with 1-vinylnaphthalene(1VN) were carried out in bulk at 65°C using 2,2′-azoisobutyronitrile(AIBN) as initiator. Reactivity ratios and distribution parameters were calculated for both systems.

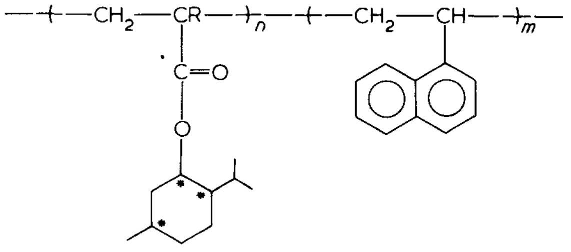
Alternating copolymers were prepared by donor–acceptor complex polymerization with $Et_3Al_2Cl_3$. The polymers were characterized by viscosity, n.m.r., i.r. and u.v. measurements. Chiroptical and fluorescence properties of the naphthalene chromophore in these copolymers are related to composition and sequence length. Possible mechanisms of optical activity induction in the naphthalene chromophore are discussed.

INTRODUCTION

Radically prepared copolymers of (−)menthyl acrylate (MtA) and (−)menthyl methacrylate(MtMA) with styrene(St), poly(MtA–co–St)s and poly(MtMA–co–St)s show a structured circular dichroism (c.d.) band centred around 262 nm[1–3], connected with the lowest energy formally forbidden ^1L_b electronic transition of the π-electron system of the phenyl chromophore[4].

In these systems, it was not possible to investigate the allowed higher energy electronic transition ^1L_a of the phenyl group situated between 205 and 230 nm[4] because of overlapping with the ester transition which is located in the same region[5].

Here we have investigated radically prepared and alternating copolymers of MtA and MtMA with 1-vinylnaphthalene(1VN). The replacement of the phenyl groups in the side chain with naphthyl groups allows us to study both ^1L_a and ^1L_b transitions as they are moved to a lower energy region between 260–320 nm[4].



R = H; poly(MtA–co–1VN)

R = H; $n = m = 1$; poly(MtA–al–1VN)

R = CH_3; poly(MtMA–co–1VN)

R = CH_3; $n = m = 1$; poly(MtMA–al–1VN)

C.d. bands related to both electronic transitions are dependent on local site symmetry and are useful for investigating the primary structure of the copolymers[6,7]. However, the ^1L_a transition has a higher oscillator strength than ^1L_b transition, and is therefore more sensitive to dipole–dipole interactions; thus it may provide additional information about the secondary structure of the macromolecules in solution[8–10].

In addition, investigation of the fluorescence spectra of the naphthalene chromophore provides a complementary insight into copolymer structure and a better correlation between chiroptical and conformational properties of the macromolecules in solution.

EXPERIMENTAL

Monomers

1-Vinylnaphthalene(1VN) (Koch–Light) was washed with 10% aqueous solution of NaOH to remove radical polymerization inhibitors, dried over anhydrous $MgSO_4$ and distilled at reduced pressure.

(−)Menthyl acrylate(MtA) and *(−)menthyl methacrylate (MtMA)* having $[\alpha]_D^{25} = -89$ (neat) and −84 (neat), respectively, were prepared and purified as reported elsewhere[3].

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Table 1 Preparation[a] and properties of poly(MtA–co–1VN)s and poly(MtA–al–1VN)

		Copolymer			
Feed 1VN(mol %)	Conversion[b] (%)	1VN units[c] (mol %)	$[\eta]$[d] (dl g^{-1})	$[\alpha]_D^{25}$ [e]	$\Delta\epsilon_{318}$ [e,f]
92.0	13.8	95.7	0.14	– 6.4	– n.d.
85.9	14.7	92.6	0.11	–10.2	– n.d.
59.8	16.0	73.2	0.13	–29.8	+0.013
28.6	7.7	50.6	0.12	–43.3	+0.015
10.0	13.6	24.0	0,10	–55.7	+0.021
2.0	26.5	4.3	0.25	–69.8	+0.051
50.0[g]	5.1	48.2	0.16	–46.7	+0.013

[a] In bulk at 65°C with AIBN as initiator, if not otherwise indicated; duration in the range 1.8–24 h

[b] Calculated as (wt polymer/wt starting comonomers) × 100

[c] Determined by n.m.r.

[d] In benzene at 30°C

[e] In chloroform

[f] Referred to one 1VN unit; ϵ expressed in $l\,mol^{-1}\,cm^{-1}$

[g] Alternating copolymer obtained by donor–acceptor complex polymerization with $Et_3Al_2Cl_3$ at room temperature in toluene

Catalysts

2,2'-Azoisobutyronitrile(AIBN) was recrystallized with ethanol before use.

$Et_3Al_2Cl_3$ was prepared by combining equimolar amount of freshly distilled Et_2AlCl and $EtAlCl_2$.

Polymerization experiments

Free radical copolymerizations were performed in bulk in dried vials. The monomers and catalysts were added under nitrogen and the vials were sealed under vacuum. After maintaining the reaction mixture at 65°C for a suitable period of time, the polymerization was stopped by pouring the bulk in large excess of methanol. The coagulated polymer was purified by dissolving in chloroform and reprecipitation in methanol several times. Finally the polymeric product was filtered and dried under vacuum.

Donor–acceptor complex polymerization was carried out in a glass apparatus with a serum cap under nitrogen atmosphere[11]. MtA or MtMA was added at –78°C under stirring in double molar excess to a toluene solution of $Et_3Al_2Cl_3$, followed by an equimolar amount of 1VN. The cooling bath was removed and the polymerization continued at room temperature under stirring; after a suitable period of time, the polymerization was stopped by pouring the reaction mixture into cold methanol containing 10% conc HCl. The coagulated polymer was purified as reported for the radically prepared copolymers.

Physicochemical measurements

60 MHz and 100 MHz n.m.r. spectra were recorded in CCl_4 solution by Varian T-60 and Jeol PS 100 spectrometers, respectively, using TMS as an internal standard.

I.r. examination of polymer samples was carried out on Perkin–Elmer Models 225 and 180 spectrometers in thin films on KBr discs, prepared from polymer solutions in $CHCl_3$ or CCl_4 by evaporating the solvents.

U.v. spectra of polymers were determined in $CHCl_3$ solution on a Cary 14 spectrophotometer in the range 240–350 nm.

Optical rotatory measurements of polymers in $CHCl_3$ solution were performed at 25°C on a Perkin–Elmer Model 141 spectropolarimeter having a sensitivity of ±0.003°. Viscosity measurements were performed with a Desreux–Bischoff dilution viscometer at 30°C in benzene.

C.d. spectra were carried out on Jobin–Yvon Dichrograph III and Cary 61 instruments in $CHCl_3$ solution in the range 240–350 nm.

Fluorescence measurements on polymer samples were performed in purified tetrahydrofuran(THF) solution. This solvent, on excitation at 280 nm, showed no emission in the wavelength range 310–520 nm of interest in this study. The concentration of solution was such to give an absorbance of approximately 0.1 at the excitation wavelength (280 nm) in a 1 cm cell.

Dry nitrogen was bubbled through the polymer solutions for 15 min to remove any dissolved oxygen, tested by spectrum intensity in relation to the bubbling time.

The fluorescence spectra were recorded with a Perkin–Elmer MPF-3L spectrofluorimeter (equipped with a 150 W xenon lamp and a R 106 Hamamatsu photomultiplier) and were followed by absorbance measurements at 280 nm with a Pye–Unicam SP 1800 spectrophotometer.

The band widths were 12 nm for excitation and 2 nm for emission. The fluorescence spectra were corrected for the wavelength dependence of the instrument response.

RESULTS AND DISCUSSION

Synthesis and characterization

The polymerization data and some of the properties of the copolymers of the systems MtA–1VN and MtMA–1VN are reported in *Tables 1* and *2*, respectively. The radically initiated copolymerization diagrams of the above two systems are shown in *Figures 1* and *2*, respectively. The reactivity ratios obtained by the modified Kelen–Tudös method[12] (in which the average monomer feed is taken for calculation purposes), are $r_{MtA} = 0.31$ and $r_{1VN} = 1.94$ for the system MtA–1VN.

For the system MtMA–1VN, the composition of the comonomers' feed is quite similar to that of the resulting copolymer in all runs. Hence, even if the conversions are, in general, higher with respect to those obtained for the previous system, the reactivity ratios can be determined by a differential method as the ratio of monomers does not change markedly during the polymerization. The values of the reactivity ratios obtained by the least square evaluation of the Kelen–Tudös parameters[13] are $r_{MtMA} = 0.54$ and r_{1VN} 0.99.

The reactivity ratios of 1VN in both systems are higher than the corresponding values for St[3], as expected from the major stability of the 1VN radical. Accordingly, MtMA has a higher value of reactivity ratio than MtA on copolymerization with both 1VN and St[3].

Table 2 Preparation[a] and properties of poly(MtMA–co–1VN)s and poly(MtMA–al–1VN)

Feed 1VN (mol %)	Conversion[b] (%)	1VN units[c] (mol %)	Copolymer		
			$[\eta]^d$ (dl g^{-1})	$[\alpha]_D^{25e}$	$\Delta\epsilon_{318}^{e,f}$
89.5	25.0	90.1	0.12	−11.4	n.d.
75.0	20.1	76.0	0.17	−28.2	+0.011
50.0	7.0	57.3	0.19	−47.0	+0.016
44.5	13.8	54.2	0.15	−48.9	n.d.
27.4	21.2	33.2	0.16	−68.0	+0.010
4.8	16.6	8.5	0.26	−86.7	+0.014
50.0[g]	20.3	49.7	0.35	−48.5	+0.027

[a] In bulk at 65°C with AIBN as initiator, if not otherwise indicated; duration in the range 1.8–25 h

[b] Calculated as (wt polymer/wt starting comonomers) × 100.

[c] Determined by n.m.r.

[d] In benzene at 30°C

[e] In chloroform

[f] Referred to one 1VN unit; ϵ expressed in mol^{-1} cm^{-1}

[g] Alternating copolymer obtained by donor–acceptor complex polymerization with $Et_3Al_2Cl_3$ at room temperature in toluene

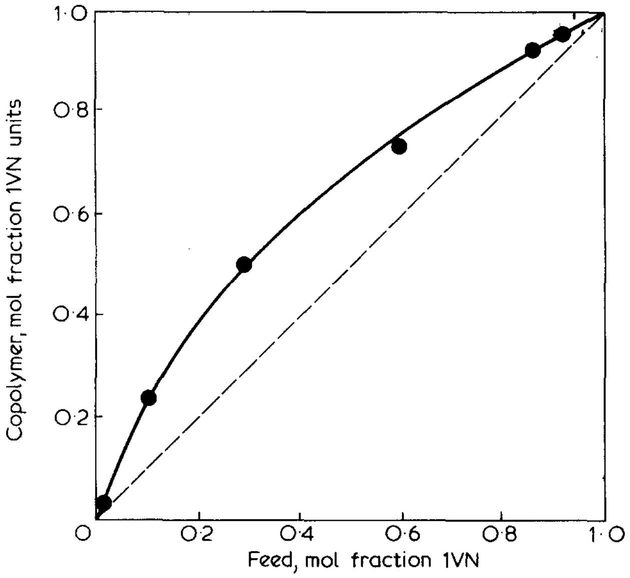

Figure 1 Copolymerization diagram for (–)menthyl acrylate (MtA)/1-vinylnaphthalene(1VN) system

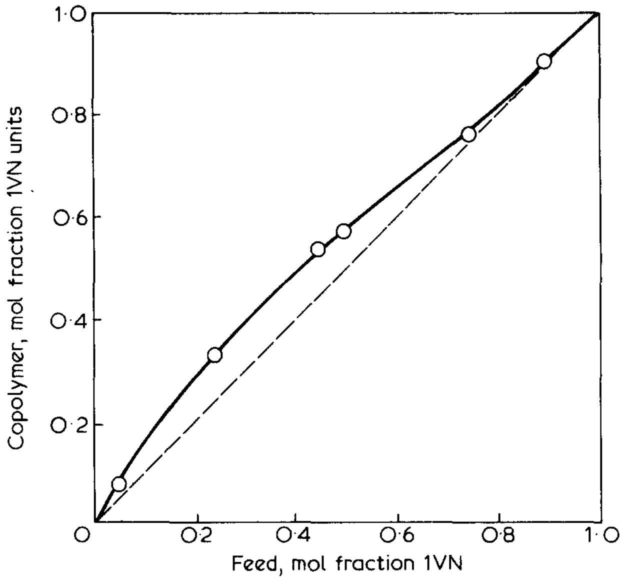

Figure 2 Copolymerization diagram for (–)menthyl methacrylate(MtMA)/1-vinylnaphthalene(1VN) system

The copolymer compositions were estimated by ^{1}H n.m.r. from the relative areas of the peaks near to 7 ppm due to the aromatic protons and 3.3–0.7 ppm due to the aliphatic protons, using the 60 MHz spectrometer when the content of 1VN units in the copolymers was higher than 20%. For copolymers containing lower amounts of 1VN units, the compositions were evaluated from the areas of the peaks near 7 and 4.5 ppm, the latter signal being due to the proton in the cyclohexyl ring closest to the ester group in MtA or MtMA units.

I.r. spectra of the poly(MtA–co–1VN)s and poly(MtMA–co–1VN)s show the same bands as the corresponding mixtures of homopolymers, indicating that both the co-units are present. Some examples of i.r. spectra of both systems are shown in *Figure 3*.

The intensity of the i.r. band at 3040 cm^{-1} due to the aromatic C–H stretching changes sharply in composition with respect to the nearby band at 2850 cm^{-1} in the region of the aliphatic C–H symmetric stretching. The logarithm of the ratio of the i.r. absorbances at 3040 and 2850 cm^{-1} (A_{3040}/A_{2850}; base line is drawn by joining the points in the spectra at 3140 and 2760 cm^{-1}) increases linearly with the content of 1VN units in the copolymer at least up to 90 mol % of 1 VN units for both the systems as shown in *Figure 4*. Therefore, the composition of an unknown copolymer sample can also be determined from the above mentioned i.r. calibration line.

Fluorescence properties

The fluorescence spectra of all the copolymers studied consist of monomer and excimer emissions centred at about 328 and 415 nm, respectively, as in poly(1VN) and in other copolymers based on 1VN[14–17]. Some typical fluorescence spectra for the MtMA–1VN system are shown in *Figure 5*.

Excimer is formed by the association of an electronically excited molecule with a ground state molecule. In earlier papers[18] it was assumed that excimer is formed only by strict parallel arrangement of aromatic rings which are separated by three carbon atoms. However, recent investigations with polymers and models suggest that excimer can be formed, even if a considerable deviation from parallel alignment is present and also if the fluorescent moieties are separated by more than three carbon atoms[19]. In fact, excimer may be formed when two far distant fluorescent groups come close by some chain folding[20]. Alternating copolymers of maleic

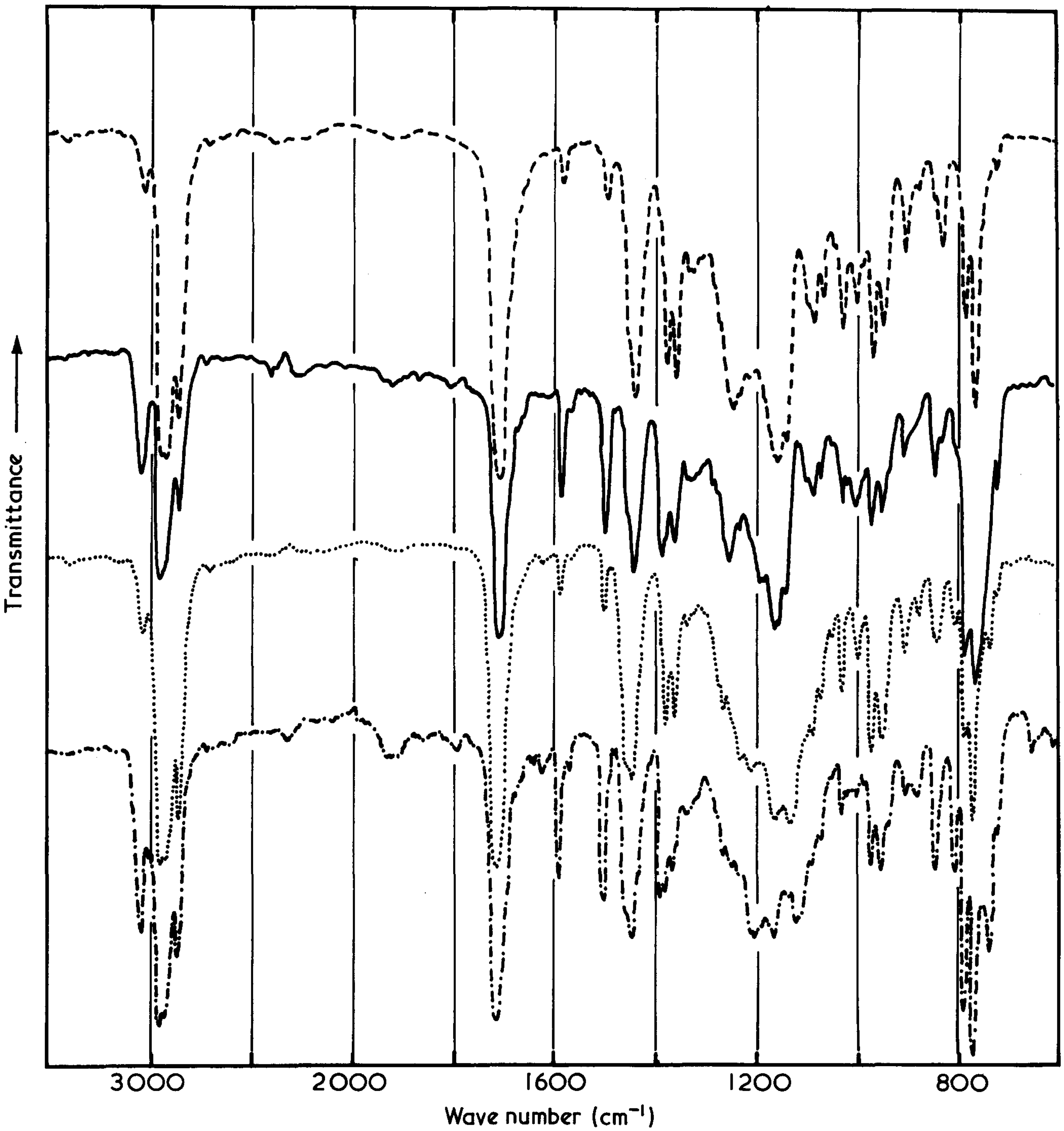

Figure 3 I.r. spectra of the radically prepared copolymers. — — — —, poly(MtA–co–1VN) with 24 mol % 1VN units; ——, poly(MtA–co–1VN) with 73.2 mol % 1VN units; · · · ·, poly(MtMA–co–1VN) with 33.2 mol % 1VN units; – · – · –, poly(MtMA–co–1VN) with 76.0 mol % of 1VN units.

anhydride with stilbene[19] or 1-vinylpyrene[20] and homopolymers of β-benzyl-L-aspartate[21] and 1-naphthyl acrylate[22] are examples which show the formation of excimers when the aromatic rings are separated by more than three carbon atoms. In some helical polymers the naphthalene rings, separated from each other by one pitch of the helical array, may also form excimers[23]. Thus, in some cases, as in poly(γ-1-naphthylmethyl-L-glutamate)[24], the relative ratio of excimer-to-monomer emission intensity (I_E/I_M) is used to determine the orientation of naphthalene rings along the chain and its conformational rigidity in a particular solvent.

In our samples, I_E/I_M was determined from the ratio of the heights of the excimer and monomer bands.

No change of I_E/I_M was observed for the absorbance at 280 nm in the 0.1–0.5 range. Hence, at the concentrations employed in our study, intermolecular excimer formation is negligible with respect to intramolecular formation.

The results of the fluorescence spectra and the distribution of monomeric units for the systems MtA–1VN and MtMA–1VN are reported in *Tables 3* and *4*, respectively.

The average sequence lengths were calculated by the method described elsewhere[25], and the fraction of links between vinylnaphthalene units ($f_{1VN-1VN}$) was evaluated from the Harwood–Ritchey run number[26].

Tables 3 and *4* clearly show that the ratio of the excimer-to-monomer fluorescence intensity increases with increasing content of vinylaromatic units in all the radically prepared copolymers. This is consistent with previous observations on other types of copolymers[14–16,27]

The formation of excimers by intramolecular association, as previously discussed, can derive from: (i) two naphthalene moieties separated by three carbon atoms; (ii) two distant naphthalene rings which come close by some chain folding.

The absence of excimer formation in an alternating copolymer suggests that excimer is formed only by mechanism (i), as reported for the alternating copolymers of *N*-vinylcarbazole with diethyl maleate[20] and of 2-vinylnaphthalene with methylmethacrylate (MMA)[28].

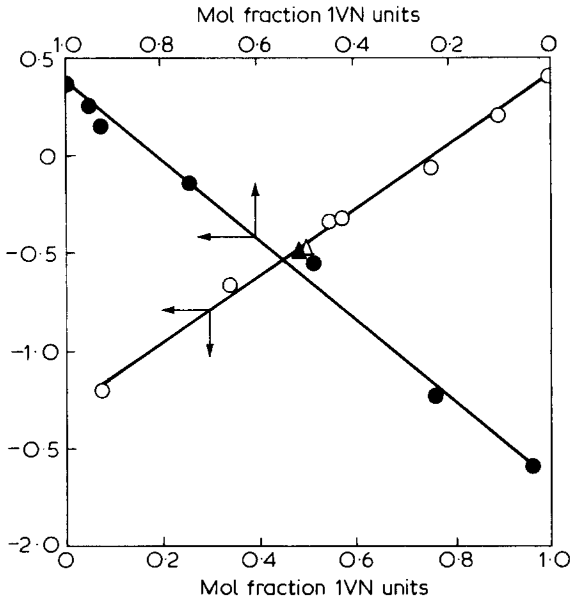

Figure 4 Logarithm of the ratio of the i.r. absorbances at 3040 and 2850 cm^{-1} *versus* composition for the systems MtA–1VN and MtMA–1VN. Radically prepared poly(MtA–co–1VN)s, ●; poly(MtMA–co–1VN)s, ○; poly(MtA–al–1VN), ▲; poly(MtMA–al–1VN), △

Poly(MtA–al–1VN) and poly(MtMA–al–1VN) show small values of I_E/I_M with respect to the corresponding radically prepared copolymers (*Tables 3* and *4*, respectively). This indicates that our copolymers are highly alternating. Some excimers in the above systems can be formed either by mechanism (ii) or by a small deviation from 100% alternating distribution. In similar donor–acceptor complex polymerization of St with MMA, some St–St diads were detected by ^{13}C n.m.r.[29].

It has been suggested that, in copolymers in which excimer formation occurs predominantly between nearest-neighbour chromophores, the ratio of excimer-to-monomer fluorescence intensity (I_E/I_M) should be proportional to the fraction of diads of fluorescent units, as observed for the system St–MMA[30].

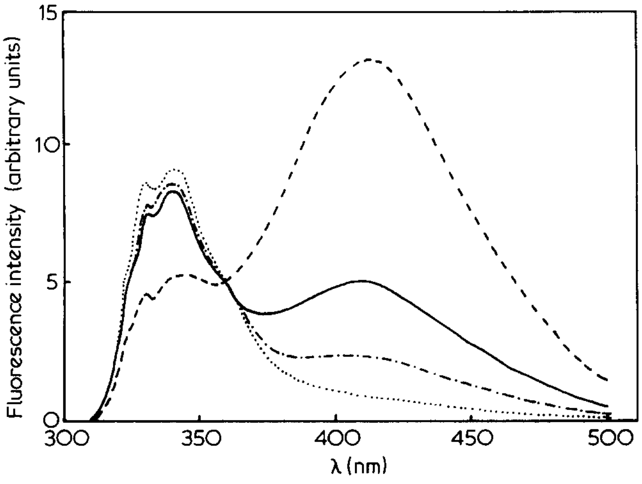

Figure 5 Fluorescence spectra in THF normalized at the same intensity at 360 nm of some radically prepared poly(MtMA–co–1VN)s having different content of 1VN units – – – –, 57.3 mol %; ———, 33.2 mol %; · · · ·, 8.5 mol %, – · – · –, poly(MtMA–al–1VN). Excitation wavelength is 280 nm

Table 3 Ratio of excimer-to-monomer fluorescence intensity (I_E/I_M) and distribution parameters for poly(MtA–co–1VN)s and poly(MtA–al–1VN)

Copolymer	1VN units (mol %)	Mean sequence length $\bar{l}_{MtA}$	$\bar{l}_{1VN}$	Run[a] number	$f_{1VN-1VN}$	$f_{1VN-1VN} \times \bar{l}_{1VN}$	I_E/I_M
Poly(MtA–co–1VN)	95.7	1.03	23.30	8.2	0.92	21.44	15
	73.2	1.22	3.74	40.4	0.53	1.98	11
	50.6	1.81	1.74	56.3	0.23	0.40	4.3
	24.0	4.19	1.19	37.2	0.05	0.06	0.66
	4.3	19.31	1.03	9.4	0.0	0.0	0.08
Poly(MtA–al–1VN)	48.2	1.00	1.00	100	0.00	0.00	0.70

[a] Average monomer feed was used for calculation purposes

Table 4 Ratio of excimer-to-monomer fluorescence intensity (I_E/I_M) and distribution parameters for poly(MtMA–co–1VN)s and poly(MtMA-al–1VN)

Copolymer	1VN units (mol %)	Mean sequence length $\bar{l}_{MtMA}$	$\bar{l}_{1VN}$	Run number	$f_{1VN-1VN}$	$f_{1VN-1VN} \times \bar{l}_{1VN}$	I_E/I_M
Poly(MtMA–co–1VN)	90.1	1.06	9.46	19.0	0.81	7.66	20
	76.0	1.18	3.97	38.8	0.57	2.26	8
	57.3	1.54	1.99	56.7	0.29	0.58	2.8
	33.2	2.43	1.37	52.6	0.07	0.10	0.64
	8.5	11.71	1.05	15.7	0.01	0.01	0.09
Poly(MtMA–al–1VN)	49.7	1.00	1.00	100	0.00	0.00	0.28

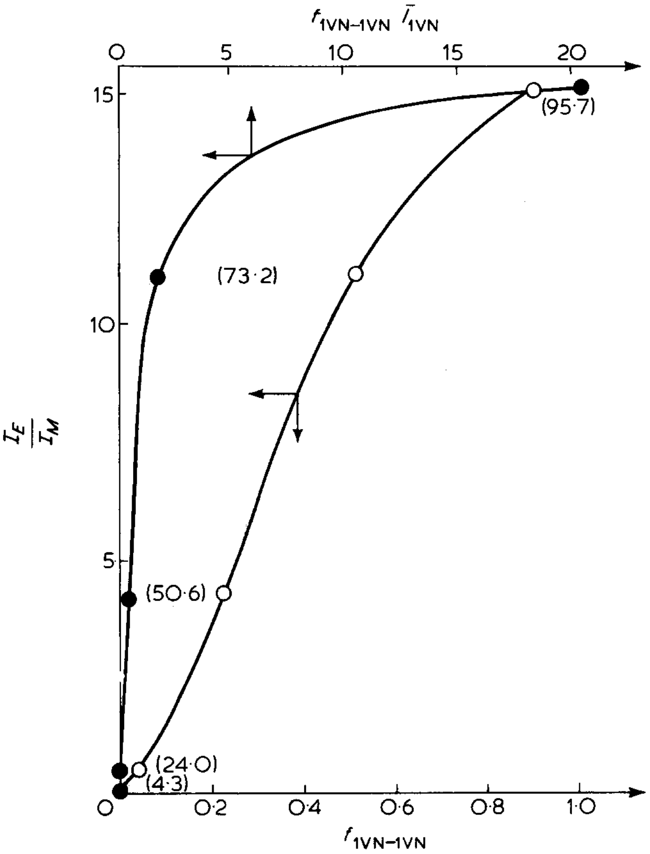

Figure 6 Dependence of ratio of excimer-to-monomer fluorescence intensity (I_E/I_M) on the fraction of links between naphthalene units ($f_{1VN-1VN}$), ○, and the product of the fraction of links between 1VN units with the mean sequence length of 1VN units ($f_{1VN-1VN}\cdot\bar{l}_{1VN}$), ●, for poly(MtA–co–1VN)s. Values in brackets are 1VN mol % contents (see *Table 3*)

However, this linear trend was successively not found to occur over a substantial copolymer composition range, not only for the system St–MMA but also for copolymers of 1VN and 2VN with MMA[17].

In agreement with these last results, the plot I_E/I_M *versus* $f_{1VN-1VN}$ for poly(MtA–co–1VN)s and poly(MtMA–co–1VN)s (*Figures 6* and *7*, respectively) is not linear. Even if the concentration of potential excimer sites is proportional to $f_{1VN-1VN}$, an initial increase in 1VN content could increase the I_E/I_M ratio due to a higher efficiency of exciton migration.

For an energy migration assumed to occur along a polymer chain by an exciton hopping mechanism involving nearest neighbours, the ratio I_E/I_M has been described as[17]:

$$I_E/I_M = k\bar{l}_f\, f_{ff}$$

where $\bar{l}_f$ = average sequence length of fluorescent units, and f_{ff} = fraction of links between fluorescent units.

This ratio should be a linear function of the product $\bar{l}_f\, f_{ff}$. This was found true experimentally in copolymers of 1VN, 2VN and St with MMA up to 83, 92 and 94 mol% of aromatic units, respectively[17].

Figures 6 and *7* show that a similar situation was observed in poly(MaT–co–1VN)s and poly(MtMA–co–1VN)s over a substantial copolymer composition range.

A lowering of the exciton migration efficiency and/or of the excimer stability would limit the above ratio. Such effects would explain the saturation observed at the highest content of 1VN units (*Figures 6* and *7*).

Chiroptical properties

The specific optical rotation of the copolymers at the sodium D line shows a linear dependence on composition for both systems (*Figure 8*), as observed for the corresponding copolymers of St[3,31].

U.v. spectra of poly(MtA–co–1VN)s and poly(MtMA–co–1VN)s in the wavelength range 260–325 nm show a low intensity band in the region between 310–325 nm and a much higher intensity band centred around 287 nm, related to the ^1L_b and ^1L_a $\pi \rightarrow \pi^*$ electronic transitions of the napththalene chromophore, respectively[4]. All the poly(MtA–co–1VN)s show a positive structured c.d. band with the maxi-

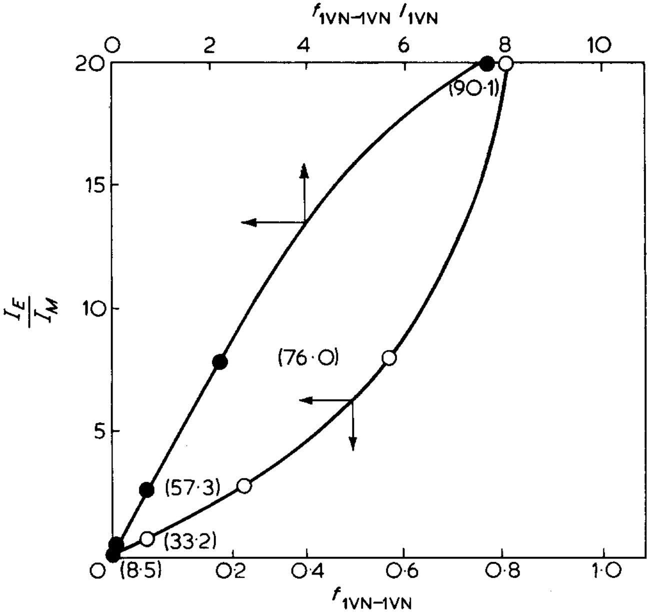

Figure 7 Dependence of the ratio of excimer-to-monomer fluorescence intensity (I_E/I_M) on the fraction of links between naphthalene units ($f_{1VN-1VN}$), ○, and on the product of the fraction of links between 1VN units with the mean sequence length of 1VN units ($f_{1VN-1VN}\cdot\bar{l}_{1VN}$), ●, for poly(MtMA–co–1VN)s. Values in brackets are 1VN mol % contents (see *Table 4*)

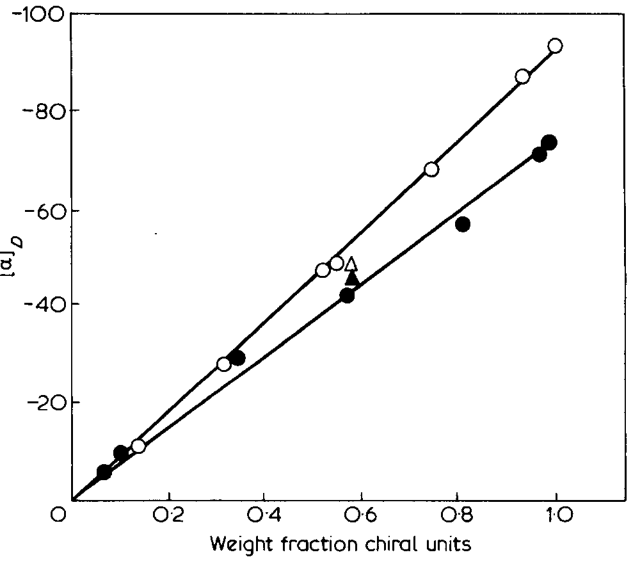

Figure 8 Specific optical rotation at the sodium D line *versus* composition for the systems MtA–1VN and MtMA–1VN. Radically prepared poly(MtA–co–1VN)s, ●; poly(MtMA–co–1VN)s, ○; poly(MtA–al–1VN), ▲; poly(MtMA–al–1VN), △

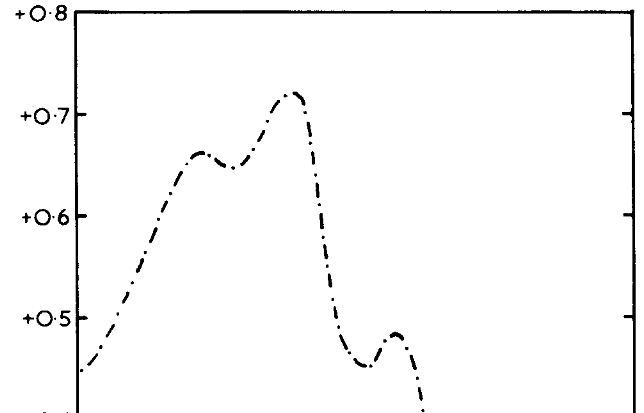

Figure 9 C.d. spectra of radically prepared poly(MtA—co—1VN)s having different content of 1VN units: — · — · —, 4.3 mol %; — · · — · · —, 24.0 mol %; — — — —, 50.6 mol %; ————, 73.2 mol %; and poly(MtA—al—1VN), · · · ·

mum near 318 nm(*Table* 1) connected with the lowest energy ^1L_b transition, whose magnitude increases with increasing content of the chiral co-unit, as observed for the corresponding St copolymers[1–3].

Poly(MtA—co—1VN)s containing less than 24 mol% of 1VN units are shown (*Figure 9*) in the 260–310 nm region connected with the ^1L_a electronic transition, a positive structured dichroic band having maxima centred at about 267, 277, 287 and 299 nm, the ellipticity of which is highest for the lowest content of 1VN units (4.3%). As the content of 1VN units increases to 50.6 and 73.2 mol%, the maximum near 277 nm reverses sign and the others remain positive. In addition, the maxima near 277 and 299 nm for poly(MtA—al—1VN) and the corresponding random poly(MtA—co—1VN) containing 50.6 mol % of 1VN units show reverse sign (*Figure 9*).

These results indicate that both ellipticity and sign of the ^1L_a dichroic band are sensitive to composition and distribution of monomeric units. The change of sign of c.d. spectra on composition also occurs for stereoregular copolymers of trytil methacrylate with (S)-α-methylbenzyl methacrylate[32].

In our case, the results can be explained tentatively by assuming that, when the content of 1VN units is lower than 24 mol %, the predominant contribution of positive sign to the ellipticity of the ^1L_a band derives from some prevailing chiral conformation of the main chain induced by long sections of chiral co-units. On the contrary, when the content of 1VN units is larger than 50%, the prevailing chiral arrangement of the main chain should decrease[33]. Thus, the local site asymmetry of naphthalene chromophore could give a reverse sign contribution to c.d. maxima at about 277 and or 299 nm. In addition, particularly in the case of poly(MtA—al—1VN) and of poly(MtA—co—1VN)s containing a rather small amount of 1VN units, negative or positive contributions to induced optical activity can arise from the interactions between optically active ester groups and naphthalene chromophores, as observed in some biopolymers[34].

Calculations on stereoregular, optically active, hydrocarbon copolymers based on 1VN have also clearly shown that c.d. of the ^1L_a band of the naphthalene chromophore is dependent both on local site asymmetry and dipole—dipole interactions[10].

The c.d. spectra in the 310–330 nm region of the radically prepared poly(MtA—co—1VN)s show, for a large range of composition, a positive structured ^1L_b band with rather low ellipticity, the maximum of the differential molar dichroic absorption at about 318 nm($\Delta\epsilon_{318}$) varying in the range + 0.010–+0.016 without any regular trend (*Table 2*). Furthermore, comparison of the c.d. band related to the ^1L_b electronic transition in poly(MtA—co—1VN)s and poly(MtMA—co—1VN)s having rather similar composition, and particularly in the samples having the lowest content of 1VN units, suggests a larger induced optical activity in the former system. Contrary to what is observed for the MtA—1VN system. poly(MtMA—al—1VN) shows the highest value of ellipticity ($\Delta\epsilon_{318} = +0.027$) (*Tables 1* and *2*). Analogous results were obtained for the corresponding copolymers of St with MtA and MtMA[3], possibly because of the presence of the α-methyl group in the MtMA units which influences syndiotactic chain propagation[35].

Investigation of the 260–310 nm spectral region has provided evidence that poly(MtMA—co—1VN) with the lowest content of 1VN units (8.5%) shows a structured ^1L_a c.d. band of negative sign (the maxima of which are centred near 267, 277, 287 and 299 nm), unlike the corresponding poly(MtA—co—1VN) (*Figure 10*). As the content of 1VN units in poly(MtMA—co—1VN)s increases, the negative ^1L_a dichroic band gradually changes sign and becomes positive (*Figure 10*). Poly(MtMA—al—1VN) shows the highest positive ellipticity.

All these data confirm that, in such systems, composition and sequence length of monomeric units markedly influence magnitude, sign, and shape of the ^1L_a dichroic band.

CONCLUSIONS

The copolymers of MtA or MtMA with 1VN show induced optical activity on the naphthalene chromophore of the side chains.

The chiroptical properties of both ^1L_b and ^1L_a electronic transitions in such systems are related to the nature of the chiral comonomer, composition and sequence length of the monomeric units.

The ^1L_a c.d. band seems to be more dependent on primary and secondary structure of the polymeric system.

The fluorescence spectra of the radically prepared copolymers show both excimer and monomer emission, the magni-

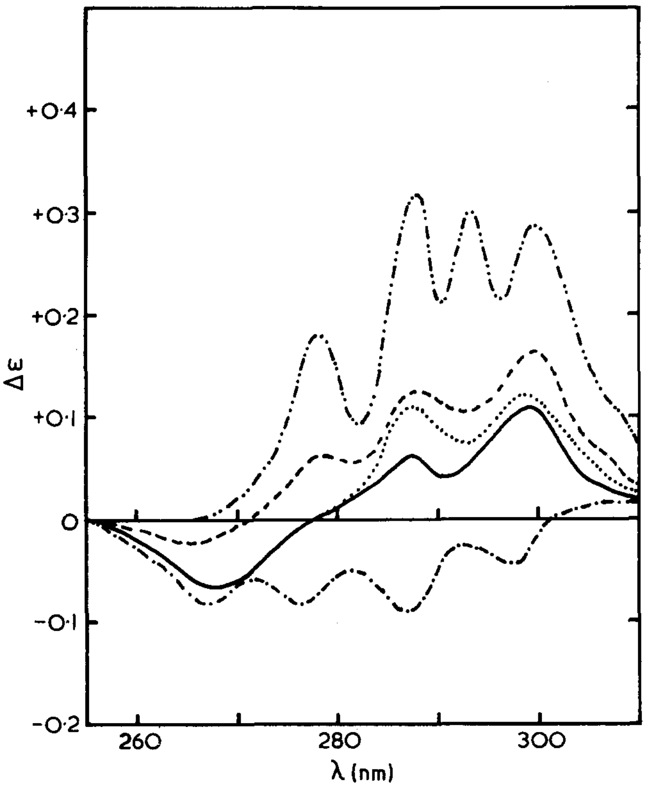

Figure 10 C.d. spectra of radically prepared poly(MaMA—co—1VN)s having different content of 1VN units: — · — · —, 8.5 mol %; ———, 32.2 mol %; — — — —, 57.3 mol %; · · · ·, 76.0 mol %; — · · — · · —, poly(MtMA—al—1VN)

tude of their intensity ratio (I_E/I_M) increasing with the content of the fluorescence co-unit in the polymers.

The polymeric products obtained by donor–acceptor complex polymerization show very low values of I_E/I_M with respect to the corresponding random copolymers of similar composition. This observation is evidence of their high alternating structure.

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