Polymer Bulletin 2, 577–587 (1980)

Optically Active Vinyl Polymers Containing Fluorescent Groups. 6.

Synthesis and Properties of Copolymers of (-)-Menthyl Acrylate and (-)-Menthyl Methacrylate with Spaced-Carbazole-Containing Monomers

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Dedicated to Prof. C.I. Simionescu on the occasion of the 60th anniversary of his birthday

Summary

Copolymers of carbazole-containing monomers such as 4- and 3-(9-carbazolylmethyl)styrene (1 and 2), 2-(9-carbazolyl)ethyl methacrylate (3) and 2-(9-carbazolylacetyloxy)ethyl methacrylate (4) with optically active menthyl acrylate (5) and methacrylate (6) were prepared by free radical polymerization.

In all cases optically active copolymers were obtained and for copolymer samples of 1 and 2 with 5 and 6, CD spectra indicate an appreciable, even if small, dissymmetric perturbation of heteroaromatic moiety.

NMR and fluorescence emission spectra of the above copolymers are consistent with a "monomer-type" behaviour which can be associated with a high dishomogeneity of the conformational environment in which the aromatic chromophores are located.

Profiles of the UV band in the 230-240nm region are analysed in terms of the different structural features of the copolymers.

^{1}H-NMR spectra recorded on partially deuterated poly(1) eliminate any contribution by the carbazolyl protons to the upfield signal (6.5-5.5ppm) of the complex aromatic protons resonance.

Introduction

The photophysical properties of optically active vinyl polymers containing aromatic units which are strongly affected by the molecular geometry, afford an extremely useful means of characterising the primary and secondary structure of macromolecules. In particular the presence of relatively small amounts of aromatic units inserted in copolymer macromolecules derived from an optically active comonomer suffices to provide a very sensitive conformational probe for the main chain, easily accessible to the presently available absorption and emission techniques. Comprehensive surveys on the

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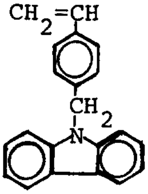
application of chiroptical properties to the conformational analysis of coisotactic copolymers of optically active α-olefins with vinylaromatic monomers such as styrene and vinylnaphthalene have been reported recently (CIARDELLI et al. 1978 and 1979).

In this contest the extension of the investigation of the chiroptical properties of copolymers of 9-vinylcarbazole with several optically active comonomers (CHIELLINI et al. 1976 and 1978a) as well as of homopolymers of optically active vinylated carbazoles (CHIELLINI et al. 1978b) was undertaken with the aim of gaining insight into the correlation between stereochemical structure and the well-known luminescence and photoelectrical properties of carbazole-containing macromolecules (HOUBEN et al. 1978).

As a part of these investigations it was of interest to obtain optically active polymers with the carbazole nucleus quite far away from the macromolecular backbone so that there is no steric interaction between the main chain and the carbazole substituent.

In the present paper results are reported concerning the synthesis and characterization of copolymers from monomers (1-4) containing the carbazole moiety well spaced from the polymerizable double bond, with (-)-menthyl acrylate (5) and (-)-menthyl methacrylate(6)



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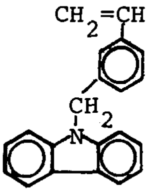

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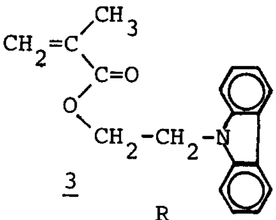

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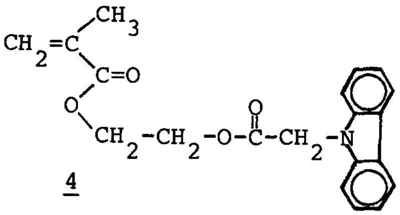

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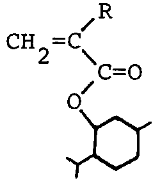

R = H 5

R = CH_3 6

Experimental

Materials

4-(9-carbazolylmethyl)styrene (1) and *3-(9-carbazolylmethyl)styrene* (2) were synthesized as previously reported (GIBSON and BAILEY 1977).

2-(9-carbazolyl)ethyl methacrylate (3) was prepared by reacting 2-(9-carbazolyl)ethanol with methacroyl chloride in THF in the presence of triethylamine (KEYANPOUR-RAD 1977).

2-(9-carbazolylacetyloxy)ethyl methacrylate (4) was obtained by reacting 9-carbazolylacetyl chloride with 2-hydroxyethyl methacrylate in THF in the presence of triethylamine (KEYANPOUR-RAD 1977).

(-)-menthyl acrylate (5) $[\alpha]_D^{25}$-89.9 (benzene) {optical purity 97.0% (SCHULZ and KAISER)} was prepared by transesterification with methyl acrylate in the presence of mentoxymagnesium bromide as previously reported (FRANK et al. 1944).

(-)-menthyl methacrylate (6) $[\alpha]_D^{25}$-91.8 (neat) {optical purity 99.0% (MENCHINI 1972)} was synthesized by reacting methacroyl chloride with (-)-menthol in pyridine in the presence of copper powder (MENCHINI 1972).

2-(4- and 3-chloromethyl phenyl)propanes mixture was prepared by reacting isopropylbenzene with chloromethyl methyl ether in the presence of $ZnCl_2$ (ZANTEN and NAUTA 1960).

2-[4-(9-carbazolylmethyl)phenyl]propane (7) was obtained under phase-transfer conditions by reacting a mixture of 2.1g (12.5mmole) of 2-(3- and 4-chloromethylphenyl)propanes, 3.6g (21.5mmole) of carbazole, 5.25ml of 50% aqueous NaOH in DMF in the presence of 0.21g (0.65 mmole) of tetra-*n*-butylammonium bromide at 60°C for 5hr The reaction mixture was poured into water and the white precipitate filtered off. The portion soluble in boiling *n*-hexane was purified by fractional crystallization from absolute ethanol, giving the less soluble *para* isomer as white needles of m.p. 103-104°C, in 63 % yield.

^{1}H-NMR ($CDCl_3$): δ = 8.2 (*m*, 2H, carbazolyl protons), 7.2(*m*,10H, carbazolyl and phenyl protons), 5.4 (*s*, 2H, CH_2 benzylic protons), 2.8 (*m*, 1H, CH benzylic proton), and 1.2ppm (*d*, 6H, CH_3).

IR showed the typical profile as derived from the overlapping of vibrations due to 9-alkylcarbazoles and 1.4-dialkylsubstituted phenyl rings.

MS: m/e 299 (M^+, 61%), 134 (13), 133 (M^+-$C_{12}H_8N$, 100) 118 (13), 117 (18), 105 (21), 91 (14).

From the mother liquors the *meta* isomer (8) was recovered by TLC with a chemical purity of 90%.

^{1}H-NMR ($CDCl_3$): δ = 8.0 (*m*, 2H, carbazolyl protons), 7.2 (*m*, 10H, carbazolyl and phenyl protons), 5.5 (*s*, 2H, CH_2 benzylic protons), 3.3 (*m*, 1H, benzylic proton), and 1.4 (*d*, 6H, CH_3).

Pentadeuterophenyl methyl ketone. 15.7g (0.118mole) of anhydrous $AlCl_3$ was slowly added, at 0°C, to a solution of 8.0g (0.097mole) of hexadeuterobenzene and 8.4g (0.108mole) of acetyl chloride in 40ml of CS_2 and the mixture was heated at 40°C for 1h. After cooling, the mixture was poured into water, extracted with $CHCl_3$ and the extracts dried over Na_2SO_4. The crude product removed from the solvent was distilled at reduced pressure to yield 1.62g (13.4%) of product having b.p. 95°C /20mmHg. The ^1H-NMR spectrum (neat) showed in the aromatic protons region two structured signals at 6.90 and 7.40ppm and a narrow singlet at 2.0ppm (CH_3CO). From the ratio H(aromatic)/H(CH_3CO) = 0.15 an isotopic purity of 92% was evaluated.

(R)(S)-1-pentadeuterophenyl-1-ethanol. A solution of 0.20g (5.3mmole) of $NaBH_4$ in 1.0ml of methanol was slowly added under stirring to a solution of 1.62g (13.0 mmole) of pentadeuterophenyl methyl ketone in 5.0ml of diethyl ether. The resulting solution was stirred for 4hr, then acidified with 10% HCl, extracted with diethyl ether, and the extracts dried overnight on Na_2SO_4. After removal of the solvents, the residue was distilled at reduced pressure to yield 1.14g (68.8%) of product having b.p. 101°C/20mmHg.

^1H-NMR (CCl_4): δ = 7.2 (*s*, 0.3H, aromatic protons), 4.7 (*q*, 1H, CH), 2.9 (*s*, 1H, OH), and 1.3ppm (*d*, 3H, CH_3).

Pentadeuterophenyl ethylene. In a 20ml Claisen flask 1.0g (7.9mmole) of (R)(S)-1-pentadeuterophenyl--1-ethanol was slowly added under vacuum to 5.0g of $KHSO_4$ preheated at 200°C and collecting all the distilling product. The distillate was dried over Na_2SO_4 and redistilled to yield 0.42g (49%) of product having b.p. 56°C/20mmHg.

^1H-NMR (neat): δ = 7.2 (*s*, 0.3H, aromatic protons), 6.6 (two *d*, 1H, CH=), 5.6 (two *d*, 1H, CH_2=), and 5.1ppm (two *d*, 1H, CH_2=).

Poly(pentadeuterophenyl ethylene). A 10ml vial containing 0.20g (1.80mmole) of pentadeuterophenyl ethylene and 2.0mg of AIBN in 2ml of benzene was sealed under vacuum and then heated at 60°C for 24hr. After cooling the solution was poured into a large excess of methanol and the coagulated polymer dried in vacuo. 0.155g of polymeric product (yield 77.5%) was obtained. The ^1H-NMR spectrum showed in the region of aromatic protons the typical profile of poly(styrene) [two broad signals at 7.1 and 6.6ppm] and a broad signal at 2.2-0.8ppm. From the ratio H(aromatic)/H(aliphatic) = = 0.12 a 93% of isotopic purity was evaluated.

Poly(4-chloromethyl-2,3,5,6-tetradeuterophenyl ethylene). A solution of 0.066g of $ZnCl_2$ in 4.6ml of chloromethyl methyl ether was added to a solution of 0.155g of poly(pentadeuterophenyl ethylene) in 7.7ml of chloromethyl methyl ether. The mixture was stirred for 24hr at room temperature and then poured into a large excess of methanol. The coagulated polymer, after reprecipitation, was dried under vacuum to yield 0.197g of polymeric product.

^{1}H-NMR ($CDCl_3$) showed broad peaks centered at δ = 7.1 (0.15H, *ortho*-aromatic protons), 6.5 (0.15H, *meta*-aromatic protons), 4.5 (2H, CH_2Cl), and 1.5ppm (3H, backbone protons).

An isotopic purity of 92.5% and 100% degree of chloromethylation were evaluated.

Poly[4-(9-carbazolylmethyl)-2,3,5,6-tetradeuterophenyl ethylene] {poly(1d4)}. 0.10g (0.64mmole) of poly(4-chloromethyl-2,3,5,6-tetradeuterophenyl ethylene), 0.15g (0.90mmole) of carbazole, 9mg ($2.8\cdot10^{-2}$mmole) of tetra-*n*-butylammonium bromide, 8.0ml of DMF and 0.3ml of 50% aqueous NaOH were heated at 60°C for 5hr. The mixture was then poured into water, extracted with chloroform and the extracts dried over Na_2SO_4. After removal of the solvents the residue was dissolved in chloroform and precipitated into methanol. The coagulated polymer was dried to yield 0.16g of polymeric product.

^{1}H-NMR ($CDCl_3$) showed broad peaks (Figure 1*d*) centered at δ = 7.9 (2H, carbazolyl protons), 7.0 (6H, carbazolyl protons), 4.9 (2H, benzylic protons), and 1.3ppm (3H, backbone protons).

A 100% degree of chlorine substitution by 9-carbazolyl groups was evaluated.

Polymerization experiments

All polymerizations were carried out under vacuum in benzene solution at 70°C for 3.5hr by using 2,2'-azobisisobutyronitrile (AIBN) as initiator. Total comonomers concentration 0.5-0.7M and a molar ratio comonomers/AIBN = 100 were used.

Polymer characterization

Copolymers composition was determined by UV {Reference absorption bands: 344nm, $\varepsilon = 4.20\cdot10^3\,l\cdot mol^{-1}cm^{-1}$ [poly(1)]; 344nm, $\varepsilon = 4.00\cdot10^3\,l\cdot mol^{-1}cm^{-1}$ [poly(2)]} and/or NMR.

Viscosity measurements were carried out in $CHCl_3$ at 30°C by using a dilution viscometer.

^{1}H-NMR spectra were recorded on a Varian T-60 or Varian XL-100 spectrometer at 37°C, using TMS as internal standard.

Optical rotatory measurements were performed on a Perkin-Elmer Mod 141 spectropolarimeter with sensitivity ±0.003°.

CD and UV spectra were recorded on a Roussell-Jouan III dichrograph and on a Cary 14 spectrophotometer respectively, on dichloromethane solution in the range 220-370nm.

Fluorescence emission spectra were recorded on outgassed solutions in dichloromethane on a Perkin-Elmer MPF-43 spectrofluorimeter at the excitation wavelength of 330nm.

IR spectra were recorded by a Perkin-Elmer Mod 180 spectrophotometer on cast films or KBr pellets.

MS spectra were recorded by a Varian MAT Mod CH7 spectrometer.

Results and Discussion

Carbazole-containing monomers 1-4 were copolymerized under free-radical conditions (initiator AIBN at 70°C) with (-)-menthyl acrylate (5) and (-)-menthyl methacrylate (6). Data relevant to the two sets of copolymerization experiments are reported in the Table.

In all cases the polymeric products, isolated as white powders, were soluble in most organic solvents and were characterized by a not very high molecular weight $\{[\eta] = 0.1\text{-}0.2 dl/g$ in $CHCl_3\}$ in accordance with previous observations for homopolymers of the corresponding vinylaromatic monomers (GIBSON and BAILEY 1977; KEYANPOUR-RAD 1977). The copolymer compositions as determined by NMR and/or UV indicated a generally higher or comparable reactivity of the 1-4 monomers with respect to the optically active ones, the larger differences being observable in the case of the copolymers with 5.

TABLE

Copolymerization of (-)-menthyl acrylate (5) and (-)-menthyl methacrylate (6) with carbazole-containing monomers 1-4 in benzene at 70°C.

Run	Comonomer Type M_1	Comonomer Type M_2	Comonomer M_2/M_1 (mol/mol)	Conv. (%)	Polymeric product Units from M_2 (mol-%)	$[\eta]$ (dl/g)	$[\alpha]_D^{25}$	$[\alpha]_o^{a)}$
A1	5	1	0.25	15.1	52.4	0.12	-27.1	-28.5
A2		2		17.8	49.5	0.09	-33.4	-30.4
A3		3		62.1	26.8	0.18	-47.2	-47.5
M1	6	1	0.25	29.4	32.5	0.10	-59.2	-59.5
M2		2		32.6	28.0	0.18	-61.3	-64.1
M3		3	0.55	65.6	36.0	0.16	-58.5	-56.2
M4		4		59.5	37.6	0.17	-51.6	-49.4

a) Evaluated for homopolymer mixtures having the same weight composition as the corresponding copolymer on the basis of $[\alpha]_D^{25}$ -70.6 (CH_2Cl_2) for poly (5) and $[\alpha]_D^{25}$ -95.6 (CH_2Cl_2) for poly(6) respectively.

IR and NMR spectra show that during the polymerization and successive treatment of samples no appreciable structural variation of monomer units occurs. In fact, IR spectra, even though complicated by the presence of different and strongly absorbing functionalities, are characterized by profiles coincident with those obtained for appropriate composites of the corresponding homopolymers.

The ^{1}H-NMR spectra of homopolymers 1 and 2 and their copolymers with 5 and 6 (Figure 1) are all characterized in the region of aromatic protons by a rather complex set of signals. However, contrary to previous suggestions (GIBSON and BAILEY 1977), it is possible to assign the contribution of the carbazolyl protons solely to the signals at 7.9 and 7.0ppm. This

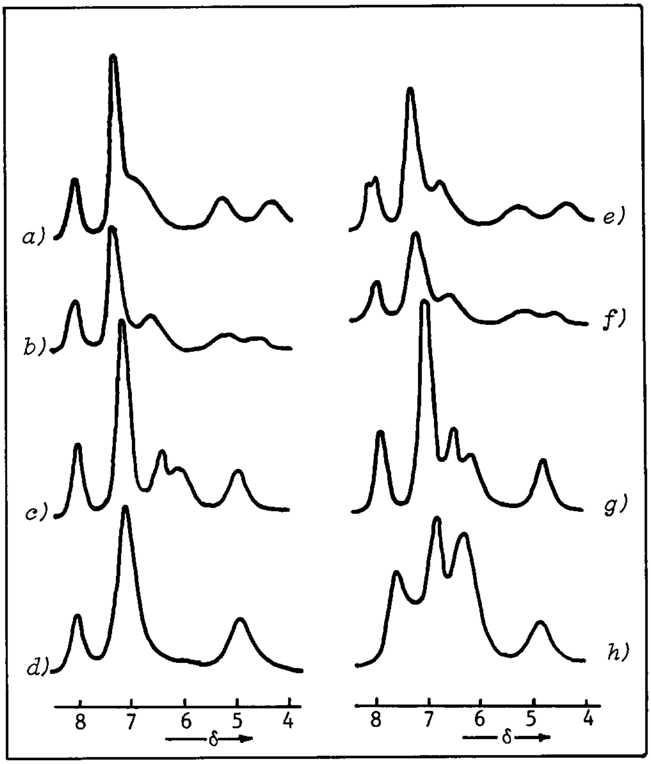

Figure 1. ^{1}H-NMR spectra in the aromatic protons region of: *a)* poly(1-*co*-6), *b)* poly(1-*co*-5), *c)* poly(1), *d)* poly(1d$_4$), *e)* poly(2-*co*-6), *f)* poly(2-*co*-5), *g)* poly(2), *h)* poly(9-vinylcarbazole).

follows since the more or less well resolved signal around 6ppm is completely missing in the spectrum of the phenyl deuterated poly(1) sample (Spectrum *d*).

It may be concluded therefore that:

i) the upfield shift of the phenyl protons observed in the reported polymers with respect to poly(styrene) (BOVEY and TIERS 1963) and poly(4-chloromethylstyrene) can be ascribed to a shielding effect of the carbazole moiety.

ii) interactions such as those claimed to be responsible for the peculiar shape of the poly(9-vinylcarbazole) resonance (Spectrum *h*) (WILLIAMS 1970), do not occur among the carbazolyl moieties of the reported polymers.

Presumably the introduction of a spacer, such as benzyl group, between the macromolecular backbone and the carbazolyl groups minimizes interactions among adjacent heteroaromatic nuclei, due to either the increased relative distance and/or conformational dishomogeneity.

The UV spectra for all the carbazolyl-containing homopolymers and copolymers in the range 350-230nm do not show any marked difference as far as position and relative intensity of the bands is concerned, confirming the expected absence of strong electronic interactions among the heteroaromatic chromophores. The 250--230nm region is however worthy of comment because of the small, but definite, differences in the shapes and intensities in the absorption bands which occur on going from low molecular weight structural models 7 and 8 to the corresponding homopolymers and copolymers (Figure 2). The effect is most pronounced in the former case (A) with the appearence of UV maximum at 230nm. In the other cases (B and C) a marked shoulder between 235 and 230nm is present.

As already reported for poly(9-vinylcarbazole), and related copolymers, the absorbance at 230nm can be associated with electronically interacting carbazolyl chromophores (CHERNOBAI et al. 1965; LEDWITH et al. 1979), similar electronic interactions must, therefore, occur in the present cases. However, origins of the interaction remain obscure, as not only hypochromism (TINOCO 1960; OKAMOTO et al. 1974) but also hyperchromism [poly(1-*co*-6) and poly(2-*co*-6)] is observed.

In contrast, the fluorescence emission spectra are in all cases the mirror images of the longest wavelength absorption band, $^1L_b \leftarrow {}^1A$ band in the Platt notation (PLATT 1949), as expected for isolated monomer species of excited carbazoles (JOHNSON 1975). The lack of excimer emission at $\lambda > 400$nm in the present series of copolymers may derive from both the occurence of only short sequences of heteroaromatic moieties and their higher flexibility consequent on the presence of a spacer between the macromolecular backbone and the emitting species.

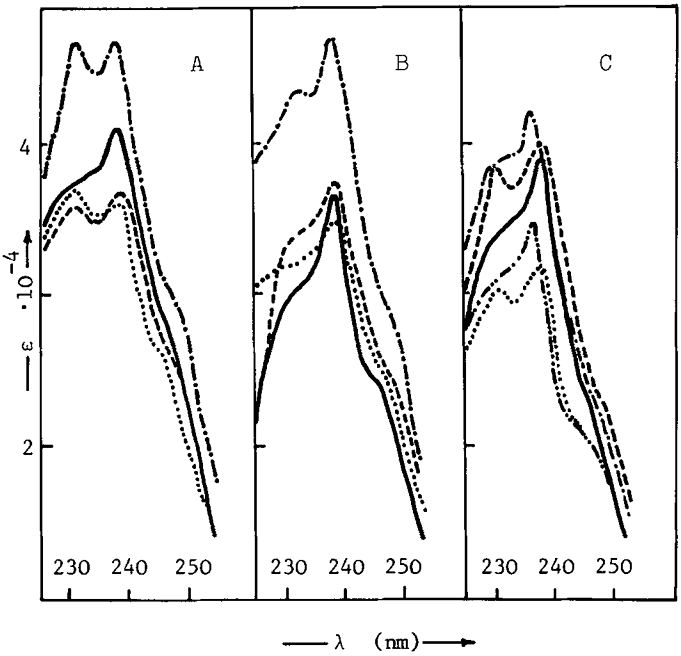

Figure 2. UV spectra in the region 255-225nm of:
A. —— 7, ··· poly(1), --- poly(1-*co*-5) and -·- poly(1-*co*-6).
B. —— 8, ··· poly(2), --- poly(2-*co*-5) and -·- poly(2-*co*-6).
C. ··· poly(3), —— poly(3-*co*-5), --- poly(3-*co*-6), -··- poly(4) and -·- poly(4-*co*-6).

This conclusion does not contrast with the fact that at least in the case of copolymers of carbazolylmethyl styrenes with (-)-menthyl acrylate and (-)-menthyl methacrylate, CD bands fitting with the UV absorption spectra of the heteroaromatic chromophore are clearly observable (Figure 3). Whilst the rotatory strengths of the dichroic bands are approximately one order of magnitude lower than those of optically active copolymers containing the carbazolyl group directly bound to the macromolecular backbone (CHIELLINI et al. 1976 and 1978a), it is nevertheless significant that induced dichroism can be observed for groups so far removed from the main chain. This result suggests that the carbazole group is a very sensitive probe for induced circular dichroism in polymers, even in those where the conformational homogeneity is too low to be detected by other spectroscopic techniques.

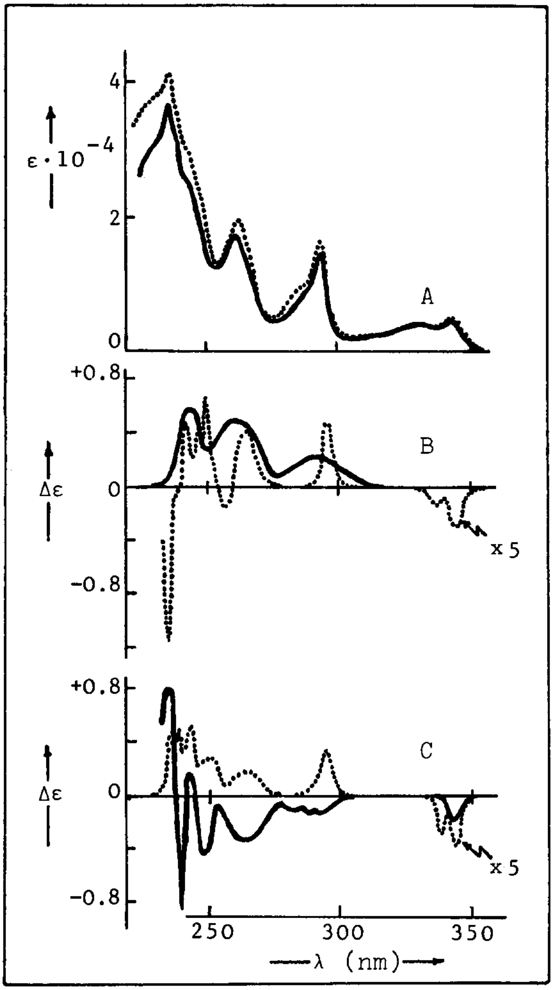

Figure 3. A. UV spectra of ··· 7 and —— 8. CD spectra of: B. ··· poly(1-*co*-5) and —— poly(2-*co*-5). C. ··· poly(1-*co*-6) and —— poly(2-*co*-6).

In order to clarify this observation, research now in progress has been extended to the characterization of coisotactic copolymers of the reported aromatic monomers (1 and 2) with other vinyl monomers, having well defined distribution of monomeric units and stereochemical order.

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Received March 27, 198o