(2) Van Aartsen, J. J.; Stein, R. S. *J. Polym. Sci., Part A-2* **1971**, *9*, 295.
(3) Stein, R. S.; Wilson, P. R. *J. Appl. Phys.* **1962**, *33*, 1914.
(4) Stein, R. S.; Wilson, P. R.; Stidham, S. N. *J. Appl. Phys.* **1963**, *34*, 46.
(5) Stein, R. S.; Rhodes, M. B.; Porter, R. S. *J. Colloid Interface Sci.* **1968**, *27*, 336.
(6) Jabarin, S. A.; Stein, R. S. *J. Phys. Chem.* **1973**, *77*, 399; **1973**, *77*, 409.
(7) de Gennes, P.-G. *C. R. Hebd. Seances Acad. Sci.* **1968**, *266*, 15.
(8) Chandrasekhar, S. "Liquid Crystals"; Cambridge University Press: Cambridge, 1977; Chapter 3.
(9) Samuels, R. J. *J. Polym. Sci., Part A-2* **1969**, *7*, 1197.
(10) Werbowyj, R. S.; Gray, D. G. *Mol. Cryst. Liq. Cryst. Lett.* **1976**, *34*, 97.
(11) Werbowyj, R. S.; Gray, D. G. *Macromolecules* **1980**, *13*, 69; **1984**, *17*, 1512.
(12) Onogi, Y.; White, J. L.; Fellers, J. F. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 663. *J. Non-Newtonian Fluid Mech.* **1980**, *7*, 121.
(13) Shimamura, K.; White, J. L.; Fellers, J. F. *J. Appl. Polym. Sci.* **1981**, *26*, 2165.
(14) Kyu, T.; Mukherjee, P., in preparation.
(15) Rhodes, M. B.; Stein, R. S. *J. Polym. Sci., Part A-2* **1969**, *7*, 1539.
(16) Hashimoto, T.; Murakami, Y.; Kawai, H. *J. Polym. Sci., Polym. Phys. Ed.*, **1975**, *13*, 1613.
(17) Prud'homme, R. E.; Bourland, L.; Natarajan, R. T.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1974**, *12*, 1955.
(18) Natarajan, R. T.; Prud'homme, R. E.; Bourland, L.; Stein, R. S. *J. Polym. Sci., Polym. Phys. Ed.* **1976**, *14*, 1541.
(19) Flory, P. J. *Proc. R. Soc. London, Ser. A* **1956**, *234*, 73.

Communications to the Editor

Heteronuclear Correlated Two-Dimensional NMR Spectroscopy Applied to the Diad Assignment of Vinyl Polymers

Nuclear magnetic resonance (NMR) spectroscopy has been widely used in past years as a practical method to analyze the configuration of polymers. Recently, two-dimensional (2D) NMR spectroscopy has been applied to this problem. Since 2D NMR experiments disperse the signals into two frequency domains, these techniques can, in principle, be used to resolve nearly degenerate resonances and make configurational assignments easier. For example, Bovey and co-workers[1] have used ^{19}F 2D *J*-correlated spectroscopy (COSY) to analyze the microstructure of poly(vinyl fluoride). Brown and co-workers have also made configurational assignments of poly(vinyl chloride)[2] and poly(vinyl alcohol)[3] by the use of ^{1}H 2D *J*-resolved experiments adapted for macromolecules (FOSY). Cheng and Lee[4] have employed ^{1}H–^{13}C heteronuclear shift-correlated 2D NMR (CSCM) to analyze the sequence distribution of ethylene–propylene copolymers. However, the use of this technique to study the configuration of polymers has not been reported. Recently, a broad-band homonuclear decoupling variation of the heteronuclear shift-correlated 2D NMR experiment (CSCMBB) has been proposed by Bax.[5] This experiment eliminates the coupling among vicinal protons in the ^{1}H domain and results in a contour plot with enhanced resolution and improved sensitivity. In this communication, we show that each of these experiments is extremely useful for the diad assignment of the methylene carbon of poly(vinylamine) (PVAm) and further suggest that these techniques may be general ones for making these assignments in other vinyl polymers.

Normally, the configurational assignments of resonances are made by comparing the polymer NMR spectrum to the spectra of model compounds or reference polymers, one with a dominant configuration. However, each of these methods is beset with difficulties. The use of model compounds may lead to wrong resonance assignments in the polymer spectrum when the polymer chemical shifts are influenced by long-range interactions and conformational effects not present in the models. Furthermore, reference polymers, if available, may have unique steric or conformational properties not present in atactic polymers which may result in chemical shift changes in certain resonances.[6] Certainly, it will be more desirable to make tacticity assignments strictly on the basis of the fundamental properties of the polymer in question. The 2D NMR approach described in this communication utilizes this feature.

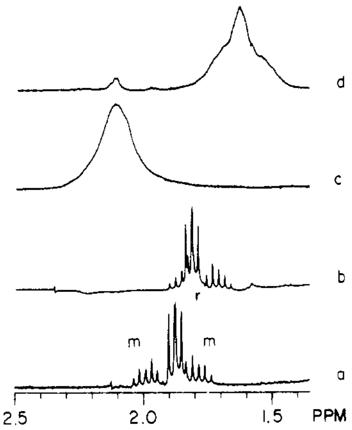
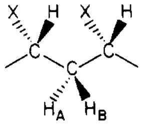
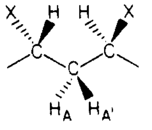


Figure 1. 300-MHz ^{1}H NMR spectra of 2,4-diaminopentane at pH 1.5 (a) and pH 8.8 (b) and of poly(vinylamine) at pH 1.5 (c) and pH 8.8 (d) in D_2O at room temperature. The 2,4-diaminopentane sample contained nearly a 1:2 mixture of meso and racemic isomers. The concentration of poly(vinylamine) was 0.05 M. Chemical shifts are referenced internally to 3-(trimethylsilyl)tetradeuterioproprionic acid sodium salt.

Results and Discussion. It has been known for years that the methylene protons of the meso (m) isomer for both model compounds and vinyl polymers are chemically nonequivalent and lead to two multiplets, while the methylene proton resonances of the racemic (r) isomer are degenerate.[6,7] For instance, the ^{1}H NMR spectra of 2,4-diaminopentane (DAP), in nearly a 1:2 molar mixture of m and r isomers at pH 1.5 (Figure 1a) and pH 8.8 (Figure 1b), illustrate these points. Two well-separated multiplets arise from the chemically nonequivalent methylene protons of *meso*-DAP. The central peaks are assigned to the methylene protons of *rac*-DAP. With increasing pH, the chemical shift difference between the two methylene m protons will become smaller but not vanish (Figure 1b). In principle, the nondegenerate methylene proton resonances can be used to determine the m and r content of vinyl polymers, as was recently shown for poly(acrylic acid)[8] as well as for other vinyl polymers.[6] Unfortunately, the ^{1}H NMR resonances of many vinyl polymers are ob-



meso diad



racemic diad

0024-9297/85/2218-2334$01.50/0 © 1985 American Chemical Society

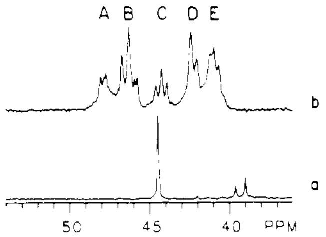


Figure 2. 75.5-MHz ^{13}C NMR spectra with proton decoupling of 2,4-diaminopentane (1:2 molar mixture of meso and racemic isomers) at pH 8.8 (a) and poly(vinylamine) at pH 8.8 (b). The concentration of poly(vinylamine) was 10% (w/v) and the spectra were internally referenced to dioxane (66.5 ppm vs. Me_4Si).

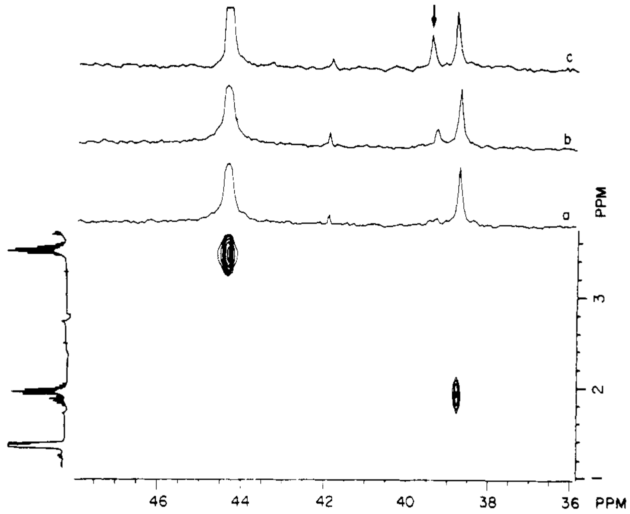


Figure 3. Contour plot from the heteronuclear correlated 2D NMR experiment with broad-band proton decoupling (CSCMBB) for a 1:2 molar mixture of meso and racemic isomers of 2,4-diaminopentane (pH 8.8). The ^{1}H NMR spectrum is above the ^{1}H axis. The projected data sets from this experiment (a) and from the heteronuclear correlated 2D NMR (CSCM) experiment (b) as well as the proton-decoupled ^{13}C NMR spectrum (c) are above the ^{13}C axis. These spectra have been scaled relative to the racemic methylene resonance for the purpose of comparison. The resonance around 41.9 ppm is an impurity.

scured due to severely overlapped resonances. This is the case for the methylene proton resonances of PVAm, where virtually one broad peak appears at both pH 1.5 (Figure 1c) and pH 8.8 (Figure 1d); even though, the methylene resonance in the ^{1}H NMR spectrum of PVAm at pH 8.8 suggest that both m and r resonances are contained within this peak (Figure 1d).

Because of the poor resolution in the ^{1}H spectra of PVAm, the tacticity of PVAm was examined by ^{13}C NMR. The optimal configurational sensitivity for PVAm was found at pH 8.8 (Figure 2b). The three most downfield regions (A, B, and C) are assigned to the methine carbon resonances displaying triad and even some pentad resolution. The two upfield regions (D and E) are the methylene carbons displaying principally diad resolution but also contain some higher order configurations. The ^{13}C NMR spectrum between 35 and 55 ppm of the DAP mixture at pH 8.8 contains only three resonances (Figure 2a; methyl resonances not shown). The resonances for the methine carbons of *meso-* and *rac*-DAP are overlapped at 44.44 ppm. The smaller downfield peak (39.55 ppm) is due to the methylene carbon of *meso*-DAP and the upfield peak (38.96 ppm) is due to this carbon in *rac*-DAP. According to the relative chemical shifts of the m and r methylene carbon resonances of the model compounds, the D peak of PVAm was initially assigned to the m diad and the upfield E peak was assigned to the r diad (Figure 2).

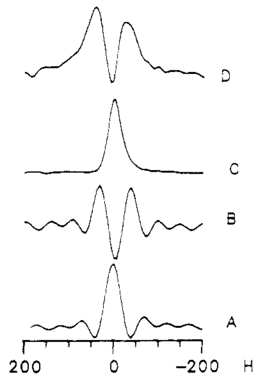


Figure 4. Cross sections parallel to the ^{1}H axis for the methylene carbons of 2,4-diaminopentane and poly(vinylamine), each at pH 8.8. The individual slices were processed from the *F*2*T*1 data set of the CSCM experiment with a double zero fill and an exponential multiplication of 10 Hz and phased to display absorption mode spectra. Spectra A and B correspond to the r and m methylene carbons of the model, respectively. Spectra C and D correspond to the D and E regions for the polymer, respectively. Since the ^{1}H chemical shifts of the model and polymer are different (Figure 1), the chemical shifts of the resonances of spectra A and C are set to 0 Hz.

In order to provide additional experimental evidence for these assignments, heteronuclear correlated 2D NMR experiments were used to examine the correlation between the carbon and proton resonances. Prior to studying PVAm, the CSCM and CSCMBB experiments were performed on the DAP mixture at pH 8.8 (Figure 3). The contour plot shows a clear correlation of the methine carbon and proton resonances in each experiment. Likewise, the upfield r methylene carbon resonance displays a cross peak with the r methylene protons. The cross section of this correlation parallel to the ^{1}H axis is shown in Figure 4a. For the methylene carbon resonance of *meso*-DAP in the CSCM experiment, a clear correlation occurred between this carbon resonance and the two nonequivalent methylene protons (Figure 4B), reconfirming the assignments of the model compound resonances. A chemical shift difference of 68 Hz is estimated from these data, which is consistent with the separation found in the one-dimensional spectrum (Figure 1b). For the CSCMBB experiment, a drastic reduction occurs in the intensity of the m methylene carbon–proton correlation (Figure 3). This fact is further reinforced in the projected data set (Figure 3a) compared to the completely decoupled ^{13}C NMR experiment (Figure 3c). Since the m methylene carbon resonance is only partially reduced as a result of the CSCM experiment (with homonuclear broad-band decoupling; Figure 3b), this suggests that the $(\pi/2, {}^{1}H)-(1/2J_{CH})-(\pi, {}^{1}H, {}^{13}C)-(1/2J_{CH})-(\pi/2, {}^{1}H)$ pulse sequence is most responsible for the loss of correlation between the m resonances.

Pines and co-workers[9] have shown that this pulse sequence, referred to as a bilinear π rotation, refocuses the proton magnetization of the carbon satellites at the chemical shift of the nonsatellite magnetization. This has a similar effect as the π ^{13}C pulsed used in the CSCM experiment.[10] The novel aspect of this pulse sequence lies in the elimination of vicinal proton coupling, hence achieving a broad-band proton-decoupled spectrum for methine carbons[5] as well as methylene and methyl carbons.[11] Optimal signal occurs when the delay value is set to $1/2J_{CH}$.[5] Error in this value decreases the intensity of the carbon–proton correlation peak.[11,12] However, since the delay used in the CSCMBB experiment on the DAP mixture was based on the measured J_{CH} value (127 Hz),

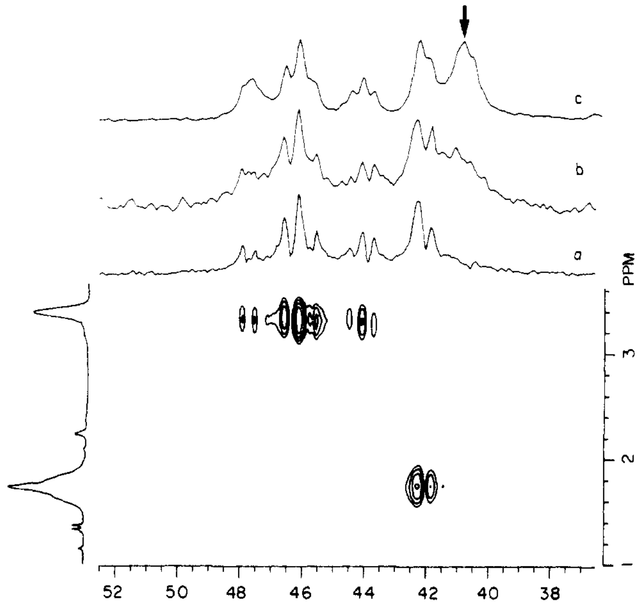


Figure 5. Contour plot from the heteronuclear correlated 2D NMR experiment with broad-band decoupling (CSCMBB) on a 10% (w/v) solution of poly(vinylamine) in D_2O at pH 8.8. The ^1H NMR spectrum is above the ^1H axis. The projected data sets from this experiment (a), the heteronuclear correlated 2D experiment without broad-band ^1H decoupling (b), and a decoupled ^{13}C NMR spectrum (c) are above the ^{13}C axis.

we do not attribute the loss of the m methylene cross peak to this condition. Two other factors can also reduce the intensity of the carbon–proton correlation. Proton multiplet widths, which are greater than 20% of J_{CH}, result in significant intensity appearing in unwanted signals at $\pm J_{CH}/2$.[11,12] The multiplet proton width of *meso*-DAP is nearly 30 Hz, which is greater than that of *rac*-DAP (15 Hz). According to Wilde and Bolton,[12] the m methylene correlation should be reduced by about 20% with respect to the r methylene correlation. Another factor that influences the intensity of these correlations is the extent of strong coupling present among the satellite protons.[9] As shown by Bolton,[13] one of the ^{13}C satellites is often strongly coupled to other protons where the chemical shift range is compressed. Since the chemical shift differences between the m methylene proton resonance is only 62 Hz (Figure 1), it is expected that, for each methylene proton, there is a strongly coupled satellite. A single bilinear π rotation pulse sequence does not refocus the magnetization from strong proton–proton coupling and results in a loss of intensity of nonequivalent protons attached to the ^{13}C nucleus.[8] Apparently, a minimum of four bilinear π pulses are needed to completely decouple protons that are strongly coupled.[8] Thus, the loss of the m methylene carbon–proton correlation is consistent with the chemical nonequivalence, large multiplet width, and probable strong coupling of these protons.

The CSCM and CSCMBB experiments were performed on PVAm at pH 8.8. For each of these experiments, a single correlation between the D methylene region and the center of the methylene protons was observed, as shown in the contour plot (Figure 5) and as a slice along the D carbon resonance parallel to the ^1H axis (Figure 4C). The E methylene region of PVAm contained two cross peaks in the CSCM experiment, separated by 63 Hz from each other (Figure 4D). Even though these resonances are not resolved in the one-dimensional experiment, the 2D approach achieved clear separation of the resonances. This separation is consistent with that found for the model compounds (Figure 4B) and indicates that the D region represents the r carbon diad resonances, while the E region contains m diad carbon resonances. Furthermore, the results of the CSCMBB experiment on PVAm indicate proton–carbon correlation for the D region is maintained, while that for the E region is much reduced (Figure 5).[14] Again, the projected data sets of the CSCMBB (Figure 5a) and the CSCM (Figure 5b) experiments as well as the normal proton decoupled ^{13}C spectrum (Figure 5c) support this fact. This assignment is contrary to the assignments proposed above from the relative chemical shifts of the model compounds.

We show that the heteronuclear correlated 2D experiments (CSCMBB and CSCM) are able to provide valuable information leading to the diad configuration assignment of PVAm. Since the phenomenon of chemically nonequivalent m protons and equivalent r protons is a general one for vinyl polymers, we suggest that these techniques may be useful for their diad assignments. In many vinyl polymers, the chemical shift differences between the m methylene protons will be sufficient to have the satellite protons not strongly coupled to each other, resulting in each 2D experiment providing two clear correlations between the m methylene carbon and proton resonances, whereas the r methylene carbon resonances should only exhibit a single cross peak. The great advantage of this technique is that the configurational assignment of vinyl polymers would rely on an intrinsic property of the polymer and can potentially be made independent of model compounds or reference polymers. A more complete configurational analysis of PVAm, based on these diad assignments, will be presented elsewhere.

Experimental Procedure. The NMR spectra were recorded with a GE 300 WB spectrometer (NT series) equipped with a 1280 computer and 293c pulse programmer. The ^{13}C NMR spectra were obtained with complete proton decoupling on 10% (w/v) solutions in D_2O at 25 °C, with dioxane as an internal chemical shift reference (66.5 ppm relative to tetramethylsilane). Pulse angles of 68° (19 μs), repetition rates of 2.5 s, sweep widths of 2100 Hz, and 2K data points were used to acquire the free induction decays. ^1H NMR spectra were obtained on 0.5 (w/v) solutions in D_2O at 25 °C. Pulse angles of 75° (8 μs), sweep widths of 900 Hz, and 8 K data points were used to acquire the free induction decays. A broad-band homonuclear decoupled heteronuclear correlation 2D NMR experiment used the following (CSCMBB) sequence:[5] $(\pi/2, {}^1H)-(t_1/2)-(\pi/2, {}^1H)-(1/2J_{CH})-(\pi, {}^1H; \pi, {}^{13}C)-(1/2J_{CH})-(\pi/2, {}^1H)-(t_1/2)-(\Delta_1)-(\pi/2, {}^1H; \pi/2, {}^{13}C)-(\Delta_2)$-(FID, decoupling). Thirty-two spectra were acquired in 12 h with the spectral width of 2K data points. Processing involved an exponential multiplication in the *F2* domain and sine multiplication and zero-filling in the *F1* domain. This produced a 1K × 64 point data set. The $\pi/2$ proton and carbon pulses were 40 and 25 μs, respectively. The delays $\Delta_1 = 4$ ms and $\Delta_2 = 1.9$ ms were used corresponding to $J_{CH} = 127$ Hz. A heteronuclear correlated 2D NMR experiment nCSCM) uses the same sequence as CSCMBB only without $(\pi/2, {}^1H)-(1/2J_{CH})-(\pi, {}^1H)-(1/2J_{CH})-(\pi/2, {}^1H)$ pulses. The parameters and processing procedures are the same as stated above for CSCMBB.

Acknowledgment. We thank Drs. C. G. Overberger and C. C. Chen, Department of Chemistry and the Macromolecular Research Center, The University of Michigan, for providing us with samples of *meso*- and *rac*-DAP andd Dynapol, Palo Alto, CA for a sample of PVAm.

Registry No. Poly(vinylamine) (homopolymer), 26336-38-9; *rac*-DAP, 29745-97-9; *meso*-DAP, 29745-96-8.

References and Notes

(1) Bruch, M. D.; Bovey, F. A.; Cais, R. E. *Macromolecules* **1984**, *17*, 2547.
(2) Macura, S.; Brown, L. R. *J. Magn. Reson.* **1983**, *53*, 529.
(3) Gippert, G. P.; Brown, L. R. *Polym. Bull.* **1984**, *11*, 585.
(4) Cheng, H. N.; Lee, G. H. *Polym. Bull.* **1984**, *12*, 463.
(5) Bax, A. *J. Magn. Reson.* **1983**, *53*, 517.
(6) Bovey, F. A. "Chain Structure and Conformation of Macromolecules"; Academic Press: New York 1982; pp 39–99.
(7) Bovey, F. A.; Hood, F. P.; Anderson, E. W.; Snyder, L. C. *J. Chem. Phys.* **1965**, *42*, 3900.
(8) Chang, C.; Muccio, D. D.; St. Pierre, T. *Macromolecules*, in press.
(9) Garbow, J. R.; Weitekamp, D. P.; Pines, A. *Chem. Phys. Lett.* **1982**, *93*, 504.
(10) Bax, A. In "Two-Dimensional Nuclear Magnetic Resonance in Liquids"; Reidel: Boston, MA, 1982; pp 50–65.
(11) Rutar, V. *J. Magn. Reson.* **1984**, *58*, 306.
(12) Wilde, J. A.; Bolton, P. H. *J. Magn. Reson.* **1984**, *59*, 343.
(13) Bolton, P. H. *J. Magn. Reson.* **1983**, *51*, 134.
(14) In the CSCMBB experiment, two resonances similar to that displayed in Figure 4D were observed, but with much reduced intensity. Furthermore, we cannot on the basis of this analysis exclude the possibility of a high-order m-centered peak contributing to the r peaks and vice versa.

C. Chang, D. D. Muccio,* and T. St. Pierre

Department of Chemistry
University of Alabama at Birmingham
Birmingham, Alabama 35294

Received July 9, 1985

Synthesis of Liquid Crystalline Side-Chain Polyitaconates via Phase-Transfer Catalysis

Scheme I

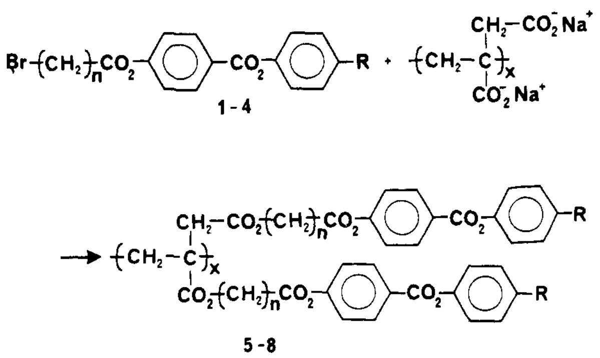


Table I
Mesomorphic Properties of ω-((Bromoalkanoyl)oxy) Esters 1-4

product	*n*	R	phase transitions[a]
1a	3	OCH_3	K 73 N 90 I
1b	4	OCH_3	K 66 N 78 I
1c	5	OCH_3	K 84 (N 82.5) I
2a	4	OC_3H_7	K 52 N 84 I
2b	5	OC_3H_7	K 71 N 95 I
3a	4	OC_4H_9	K 64 N 87 I
3b	5	OC_4H_9	K 47 N 85 I
4a	4	C_6H_5	K 114 N 138 I
4b	5	C_6H_5	K 133 N 141 I

[a] Transition temperatures in °C; K = crystal, N = nematic, I = isotropic.

During recent years, increasing interest has been shown in thermotropic liquid crystalline polymers.[1-5] This interest is justified both by the potential technological applications of these materials and by the fundamental problems they give rise to.

Thermotropic liquid crystalline polymers are classified under two categories: "main-chain" and "side-chain" polymers. In the first, the liquid crystalline character is a property of the chain backbone; i.e., the mesogenic groups are linked to form the macromolecular chain. In the side-chain liquid crystalline polymers, with which this work deals, low molar mass mesogenic groups are linked to the polymeric chain as side chain directly or via flexible spacers.

The systematic synthesis of liquid crystalline side-chain polymers has become possible by applying the "flexible spacer concept" originally proposed by Finkelmann et al.[6], which postulates a partial decoupling of the motion of the polymer main chain from the motion of the anisotropically oriented mesogenic side chains. By this means, a few series of mesomorphic polymers have been prepared by varying the chemical constitution of the macromolecular backbone: polymethacrylates,[6] polyacrylates,[7] poly(chloroacrylates),[8] and polysiloxanes.[9-12] But even though mesogenic side-chain polymers have been synthesized and investigated for several years, the mutual interaction of polymeric and liquid crystalline properties is not well understood. Therefore, new series of liquid crystalline side-chain polymers are needed in order to diversify the structures of the compounds available. This might help to better understand the influence of the main chain on the liquid crystalline properties of the side-chain polymers.

We wish to present here the synthesis and the phase behavior of a new series of liquid crystalline polymers with a polyitaconate backbone.

Results and Discussion. Liquid crystalline side-chain polymers are usually prepared by the radical polymerization of appropriate mesogenic monomers such as acrylates,[7] methacrylates,[6] or chloroacrylates.[8] However, another synthesis route has been proposed, starting with "reactive polymers"[9-13,19] which can be modified to mesogenic side-chain polymers by using suitable reactive mesogenic compounds.

Following this route, we have recently described a new synthesis of mesomorphic polyacrylates[14] resulting from the reaction of sodium polyacrylates with mesogenic ω-((bromoalkanoyl)oxy) esters under phase-transfer conditions.

The synthesis of the liquid crystalline polyitaconates **5–8** is similar to this published procedure. It is achieved by displacement of bromide ion from ω-((bromoalkanoyl)oxy) esters **1–4** with sodium polyitaconates under phase-transfer conditions (Scheme I). The ω-((bromoalkanoyl)oxy) esters **1–4** are heated under reflux in water–chloroform solvent with sodium polyitaconates and tetrabutylammonium bromide as phase-transfer reagent. Mesomorphic polyitaconates are recovered from chloroform solution by precipitation with methanol as nonsolvent (see experimental part).

The melting and transition points for the ω-((bromoalkanoyl)oxy) esters **1–4** are reported in Table I, while Table II lists the polymers synthesized (**5–8**), with yields, inherent viscosities (in chloroform at 25 °C), and thermal properties.

In these experiments, we have not tried to optimize the parameters (solvents, structures of the phase-transfer reagents, and molar ratio between the ω-(bromoalkanoyl)oxy esters and the reactive groups of the polymer) with respect to yields. However, the completion of the alkylation reaction was confirmed by the IR spectra of the polymers. For example, a comparative study of the IR spectra of the starting polymer (Figure 1, curve A) and of the polyitaconates **6b** (Figure 1, curve B), **7b**, and **8a** (Figure 2, curves A and B) shows that only ester carbonyl

0024-9297/85/2218-2337$01.50/0 © 1985 American Chemical Society