erization technique, which presumedly gives rise to strictly alternating copolymers.

Our finding that poly(BPA–iminocarbonate) can be prepared directly from BPA and cyanogen bromide is significant for the evaluation of poly(iminocarbonates) for possible large-scale industrial applications. Since the separate isolation and purification of the reactive dicyanates can be circumvented, the cost associated with the industrial-scale production of poly(BPA–iminocarbonate) should be comparable to the cost of the widely used poly(BPA–carbonate).

We prepared four structurally new poly(iminocarbonates), using polymerization procedures that had been optimized for BPA. All tested diphenols with the exception of the ortho-substituted 2,2′-dihydroxyazobenzene polymerized readily. Since the obtained polymers had lower molecular weights than poly(BPA–iminocarbonate), the synthetic procedures, although generally applicable, require careful optimization for each specific diphenol, in order to afford polymers with molecular weights above 50 000.

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Registry No. (BPA)(BPA dicyanate) (copolymer), 26025-74-1; (BPA)(BPA dicyanate) (SRU), 26101-32-6; (BPA)(cyanogen bromide) (copolymer), 118798-91-7; (TDP)(BPA dicyanate) (copolymer), 118798-92-8; (TDP)(BPA dicyanate) (SRU), 118798-96-2; (CTTH)(BPA dicyanate) (copolymer), 118798-95-1; (BPA dicyanate)(Dat-Tym) (copolymer), 118798-94-0; potassium *tert*-butoxide, 865-47-4; tetrabutylammonium bromide, 1643-19-2.

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Synthesis of Thermotropic Liquid Crystalline Side-Chain Polymers via Chemical Modification of Polymeric Carboxylic Acids

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ABSTRACT: Esterification of poly(acrylic acid) and poly(methacrylic acid) with relatively bulky alkyl halides via the corresponding tetrabutylammonium salts in dimethylformamide was conducted by following three different procedures. The following observations were made: (1) the presence of methanol and water was detrimental to the desired reaction on the polymeric substrate, (2) the excess tetrabutylammonium hydroxide in the presence of a small amount of water caused the hydrolysis of base-sensitive alkylating agents, and (3) residual water accompanying polymeric carboxylate was conducive to the enhancement of the degree of substitution and product yield for alkylating agents that can survive the basic condition. For the base-sensitive alkylating agent, it is essential that residual tetrabutylammonium hydroxide be removed. The product showed liquid crystallinity with a degree of substitution as low as 25% for the polyacrylate backbone. For the stiffer polymethacrylate backbone, a degree of substitution of at least 40% is needed for mesophase formation.

I. Introduction

Since Finkelmann and Ringsdorf[1,2] first proposed the idea of inserting a flexible spacer between a polymer backbone and a mesogenic group to induce liquid crystal formation in a polymeric system, voluminous publications have appeared to date on the synthesis of liquid crystalline side-chain polymers. Of all the backbone structures that have been synthesized, polyacrylate and polymethacrylate are by far the most extensively studied.[3-7] Both acrylate- and methacrylate-based liquid crystalline polymers can, in principle, be synthesized either by direct polymerization of appropriate monomers or by chemically modifying poly(acrylic acid) and poly(methacrylic acid). The chemical modification approach has a distinctive advantage in that a wide range of narrowly defined chain lengths can be realized by the commercial availability of parent polymeric carboxylic acids. Moreover, liquid crystalline polymers with high stereochemical purity can be achieved.[8] These two features are particularly important in furnishing liquid crystalline polymers with well-defined structures for the elucidation of structure–property relationship.

There are several approaches to the synthesis of mesomorphic polyacrylate and polymethacrylate by way of

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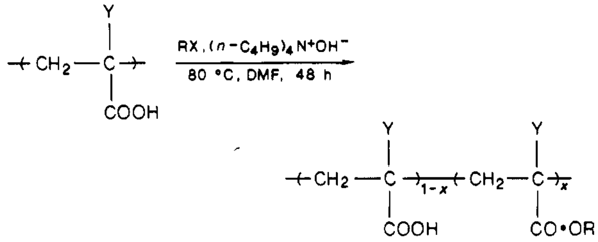
chemical modification. In a recent series of communications, Keller[9-11] has presented the use of liquid–liquid and solid–liquid phase-transfer-catalyzed (PTC) reactions for the chemical modification of poly(sodium acrylate) and poly(sodium methacrylate). However, the PTC reactions do not appear to be attractive partly because of the possibility of being predominated by side reactions[12] and partly because of low yield.[11] Nucleophilic substitution between poly(sodium acrylate), PSA, and a liquid crystal mesogen has also been carried out in hexamethylphosphoramide, HMPA, to avoid the problem of side reactions.[13] Although there was supportive evidence for the formation of mesomorphic polyacrylate, the yield was found to be no more than 20%. This could be attributed to relatively low solubility of PSA in HMPA and to relatively low reactivity of the carboxylate group due to the compact and hence tightly bound counterion (i.e., Na^+). Hence, as one of the solutions, one should look to the bulkier and hence more loosely bound counterion for the improvement of product yield; tetrabutylammonium ion seems to be a logical choice. As a matter of fact, Cohen[14] and Bailey et al.[15] have successfully conducted reactions on poly(methacrylic acid) with the aid of tetrabutylammonium hydroxide in polar aprotic solvents, such as dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), although the scope of their investigations was mostly limited to alkylating agents with relatively simple molecular structures. It was the objective of this work to extend Cohen's strategy[14] to liquid crystal mesogens as alkylating agents in the hope of arriving at a set of conditions that give rise to optimal yield of mesomorphic polyacrylate and polymethacrylate.

II. Results and Discussion

The general scheme of reaction examined in the present work is



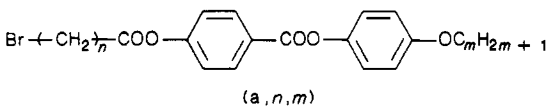
$$\left(CH_2-\overset{\overset{\Large Y}{|}}{\underset{\underset{\Large COOH}{|}}{C}}\right) \xrightarrow[80\ °C,\ DMF,\ 48\ h]{RX,\ (n\text{-}C_4H_9)_4N^+OH^-} \left(CH_2-\overset{\overset{\Large Y}{|}}{\underset{\underset{\Large COOH}{|}}{C}}\right)_{1-x}\left(CH_2-\overset{\overset{\Large Y}{|}}{\underset{\underset{\Large CO\cdot OR}{|}}{C}}\right)_x \quad (1)$$

where homopolymeric poly(acrylic acid) and poly(methacrylic acid) with Y = H and CH_3, respectively, were alkylated with the assistance of tetrabutylammonium hydroxide (TBAH) in DMF, and the degree of substitution is designated by subscript x. We chose to work with DMF because our tests showed no advantages of DMSO or HMPA over DMF as reaction media insofar as the degree of substitution and product yield are concerned. Besides the present experimental procedures, as detailed in section IV, the procedures devised by Cohen[14] and Bailey et al.[15] were also followed, and the results compared to each other. In Cohen's procedure, poly(methacrylic acid) was mixed with TBAH and an alkylating agent without the isolation of poly(tetrabutylammonium methacrylate). In the procedure formulated by Bailey et al., a methanol solution of poly(methacrylic acid) was neutralized with 4 mol % excess of TBAH, also in methanol, and poly(tetrabutylammonium methacrylate) was obtained by the evaporation of methanol and water under reduced pressure; no effort was made to remove the excess TBAH. The reaction was then carried out in DMSO. In contrast, our method involved the precipitation of the tetrabutylammonium salts of polymeric carboxylic acids (formed upon acid–base neutralization) in an excess of diethyl ether, thereby removing unconsumed TBAH. TBAH was found to be highly soluble in diethyl ether via an independent experiment. The alkylating agents used here include two classes of liquid crystal mesogens

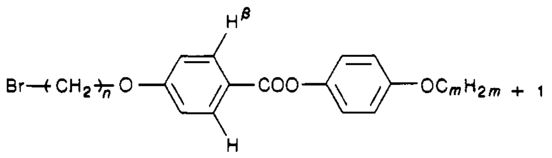
Table I
Thermal Properties of (a,n,m), (b,n,m), and (c,n)

compd	T (K → I)[a]	T (K → N)[a]	T (N → I)[a]
(a,5,4)		59.9 (47)[b]	80.8 (85)[b]
(a,5,1)	93.1 (84)[b]		72.1[c] (82.5)[b,c]
(a,10,4)		75.7	88.8
(a,10,1)	80.0		
(b,2,4)	114.7		
(b,6,4)		75.7 (71)[d]	96.2 (80.5)[d]
(b,6,1)	79.5 (78)[d]		71.0[c] (75.5)[c,d]
(c,5)	118.0 (120)[e]		
(c,10)	97.0 (99)[e]		

[a] K, crystalline; N, nematic; I, isotropic; T in °C. [b] Reference 9. [c] Monotropic behavior, T (I → N) reported. [d] Reference 11. [e] Reference 16.

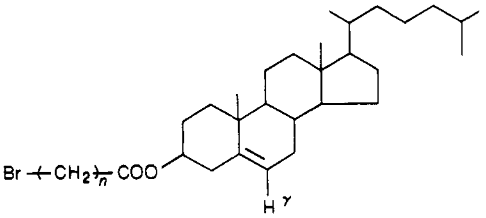


(a,n,m)



(b,n,m)

and nonmesogenic cholesteryl derivatives.



(c,n)

It is noted that (a,n,m) and (b,n,m) are similar in their mesomorphic behavior; both may show nematic and possibly smectic mesophases depending on the length of the spacer and tail groups.[9,10] There is, however, a major difference expected of these two mesogens in that (a,n,m) was found to be susceptible to hydrolysis under basic conditions[12] whereas (b,n,m) should be more stable to the same conditions for lack of an activated ester linkage. This is one of the issues that were addressed in this work. Compounds (c,5) and (c,10) under present investigation are both crystalline as observed by Shannon.[16] The thermal properties of all three classes of compounds under present investigation are summarized in Table I; the reported transition temperatures were determined with differential scanning calorimetry in conjunction with hot-stage polarizing optical microscopy.

As a general observation, we note that Cohen's procedure carried out at 60 °C did not result in the desired polymer product according to eq 1 with mesogen (a,n,m) or (b,n,m), the former appearing to have decomposed on the basis of proton NMR spectra, while the latter produced no product at all. To ensure that the reaction was performed properly, we also used iodomethane and benzyl bromide as alkylating agents, both giving rise to essentially complete degree of substitution and a product yield of about 50%, which is consistent with Cohen's observation.[14] The complete

Table II
Properties of Chemically Modified Polyacrylate

alkylating agent	glass transition T_g (midpoint), °C	clearing point T_i (max), °C	mesophase	method	degree of substitution, %	product yield, %
(a,10,4)	46	136	smectic(106), nematic	present study	25	37
(a,10,1)	51	100	nematic	present study	27	43
(a,5,4)	62	120	nematic	present study	35	44
(a,5,1)	63		no	present study	37	45
(b,2,4)	61	100	nematic	ref 15	55	64
(b,6,1)	41	110	nematic	ref 15	60	58
(b,6,4)	31	125	nematic	ref 15	66	66

Table III
Properties of Chemically Modified Polymethacrylate

alkylating agent	glass transition T_g (midpoint), °C	clearing point T_i (max), °C	mesophase	method	degree of substitution, %	product yield, %
(a,10,4)	54		no	present study	20	39
(a,10,1)	42		no	present study	30	42
(a,5,4)	68		no	present study	35	45
(a,5,1)	59		no	present study	35	38
(b,2,4)	88		no	present study	40	45
(b,2,4)	78		no	ref 15	55	62
(b,6,1)	47	76	nematic	ref 15	60	65
(b,6,4)	38	102	nematic	ref 15	60	60
70% (b,6,4) + 30% (c,10)	43	74	nematic	ref 15	40	58
30% (b,6,4) + 70% (c,10)	45		no	ref 15	30	63

substitution was ascertained by IR spectroscopy and the integration of relevant proton NMR signals. In contrast, the procedure of Bailey et al. conducted in DMF at 80 °C was found to conform to Scheme I for mesogen (b,*n*,*m*) with a degree of substitution of 55–65% and a product yield of 60%. However, the procedure failed for mesogen (a,*n*,*m*) to proceed as stated in eq 1. In retrospect, the failure of Cohen's method with (b,*n*,*m*) might have been due to the reduced reactivity of carboxylate groups in the presence of methanol and water. The present procedure, in which the slight excess of TBAH was removed by precipitation of the tetrabutylammonium salt of poly(acrylic acid) or poly(methacrylic acid) with diethyl ether, was found to conform to eq 1 even for base-sensitive (a,*n*,*m*) with a degree of substitution of 25–40% and a product yield around 40%.

As a basis for the comparison of effectiveness, (b,2,4) was chosen to react with poly(tetrabutylammonium methacrylate) following the present procedure and that of Bailey et al.[15] It was found that the latter procedure resulted in a higher degree of substitution than the former, 55% as opposed to 40%. It appears that the slight excess of TBAH remaining with the polymeric carboxylate in accordance with the method of Bailey et al. has played a major role. The presence of TBAH might have catalyzed the hydrolysis of mesogen (a,*n*,*m*) at the activated α position as noted in one of our earlier studies,[12] leading to the failure of eq 1 to proceed. The small amount of water present in the procedure of Bailey et al. might have led to the following two observations: (1) Once catalyzed by the excess TBAH, the hydrolysis of (a,*n*,*m*) is expected to be sustained with residual water. (2) The relatively wet system has contributed to the enhanced rate of the alkylation of carboxylate in view of Zahalka and Sasson's study of the role of water in solid–liquid phase-transfer reactions.[17] The result is that a higher degree of substitution and a higher product yield were both achieved than what one could accomplish with the present procedure. The trade-off of this advantage is that the labile alkylating agent, such as mesogen (a,*n*,*m*), may not survive the prevailing basic condition.

Using the data reported in Tables II and III, we make the following observations on the temperature range of mesophase formation in relation to the degree of substitution, spacer length, and tail group: (1) With the polyacrylate backbone, a nematic mesophase was observed for degrees of substitution as low as 25% excepting the polymer product with mesogen (a,5,1). In contrast, no mesophase was observed for polymethacrylate backbone with a degree of substitution less than 40%. It is also noted that roughly the same degrees of substitution were achieved for polyacrylate and polymethacrylate with a given mesogen. One plausible explanation is that the propensity to mesophase formation increases with increasing backbone flexibility, which has literally no effect on the reactivity of carboxylate groups. (2) The temperature range of mesomorphism, namely, $T_i - T_g$, increases with the length of the spacer group and the length of the tail group.

Finally, we also tested the idea of synthesizing copolymers by reacting (b,6,4) and (c,10) with poly(tetrabutylammonium methacrylate) following the procedure of Bailey et al.[15] The composition of (b,6,4) vs (c,10) in the resultant polymer product was determined by the integration of the NMR signals for protons designated as β and γ in formulas (b,*n*,*m*) and (c,*n*), respectively. For the molar ratio (b,6,4):(c,10) equal to 7:3, the polymer product was found to comprise better than a factor of 10 in favor of (b,6,4). However, for the ratio 3:7 charged to the reactor, both alkylating agents accounted for about 50% each in the product. Other characteristics of both polymer products are listed at the bottom of Table III. It is evident that the introduction of the bulkier (c,10) into the backbone as side groups has reduced the overall degree of substitution from 60% with (b,6,4) alone to 30–40%. Furthermore, in view of the fact that the three alkylating agents studied here are all relatively bulky, there is little surprise that complete conversion (i.e., 100% degree of substitution) was not achieved in any of the reactions listed in Tables II and III. In sharp contrast, essentially complete substitution was observed with relatively compact iodomethane and benzyl bromide as alkylating agents.

III. Summary

The esterification of poly(acrylic acid) and poly(methacrylic acid) was carried out with the assistance of tetrabutylammonium hydroxide in dimethyl formamide. A comparative study was made between the three different procedures in which poly(tetrabutylammonium acrylate) and poly(tetrabutylammonium methacrylate) were prepared. With the three alkylating agents, it was found that the procedure of Bailey et al. resulted in a higher degree of substitution and a higher product yield than the present procedure for (b,*n*,*m*), presumably because of the presence of catalytic amount of water accompanying the polymeric carboxylate. However, compound (a,*n*,*m*), which is susceptible to base-catalyzed hydrolysis, failed to conform to the desired reaction pathway as the procedure of Bailey et al. was followed. The presently proposed procedure, in which residual tetrabutylammonium hydroxide, solvent methanol, and water were all removed, was found to be satisfactory for both (a,*n*,*m*) and (b,*n*,*m*). The feasibility of synthesizing copolymers by using (b,6,4) and (c,10) was also explored. It was found that the introduction of the bulky (c,10) as side groups tends to depress the degree of substitution compared to using (b,6,4) alone. On the basis of the information gathered for the systems studied in the present work, we found that the more flexible polyacrylate backbone (compared to polymethacrylate) is more prone to liquid crystal formation. Moreover, the temperature range for mesophase formation increases with the length of spacer or tail group.

IV. Experimental Section

1. Synthesis of (a,*n*,*m*), (b,*n*,*m*), and (c,*n*). (a,*n*,*m*) was synthesized according to formerly reported procedures,[12] (b,*n*,*m*) in accordance with Keller's procedures,[10] and (c,*n*) with Shannon's procedures.[16]

2. Synthesis of Poly(tetrabutylammonium acrylate), PTBAA, and Poly(tetrabutylammonium methacrylate), PTBAM. Poly(acrylic acid), PAA, with approximate molecular weight 250 000 was used as received from Scientific Polymer Products. Poly(methacrylic acid), PMA, was purchased from Polysciences, Inc. Iodomethane was used to convert PMA to PMMA following Cohen's procedure.[14] The intrinsic viscosity of the resultant PMMA in chloroform at 39 °C, determined with capillary viscometry, was then used to arrive at $\bar{M}_n = 130\,000$ by using the Mark–Houwink–Sakurada constants listed for PMMA with applicable molecular weight range under the same conditions of temperature and solvent.[18]

To PAA or PMA (2.33×10^{-3} mol in carboxylic groups) in methanol was added 2.6 mL of methanol solution of TBAH (1 M, Aldrich Chemical Co.). The mixture was stirred at 60 °C for 24 h. PTBAA and PTBAM was then isolated by precipitation from the methanol solution with an excess of diethyl ether. The precipitate was then dried at reduced pressure for 24 h.

3. Reaction of (a,*n*,*m*) and (b,*n*,*m*) with PTBAA and PTBAM in DMF. The PTBAA or PTBAM samples prepared above were dissolved in 20 mL of DMF, to which 10 mL of DMF solution of (a,*n*,*m*) or (b,*n*,*m*) (2.60×10^{-3} mol) was added. The reaction mixture was stirred at 80 °C for 48 h. The product was isolated by precipitation from the DMF solution with 250 mL of methanol. The white product was redissolved in chloroform and then precipitated again with methanol. The final product was collected with a centrifuge and dried in a vacuum oven. It was further verified that the product precipitated twice with 0.2N HCl aqueous solution showed identical NMR spectra without any signals due to the tetrabutylammonium group, confirming that the unconverted portion of PTBAA or PTBAM was indeed carboxylic acid as depicted in Scheme I. The product yield was calculated based on the weights of PAA and PMA used in part 2 for the preparation of PTBAA and PTBAM, respectively.

4. Reaction of (b,6,4) and (c,10) with PTBAM in DMF. In the case of (b,6,4):(c,10) = 3:7, 6.99×10^{-4} mol of (b,6,4) in 10 mL of DMF was mixed with 10 mL of a DMF solution of 2.33×10^{-3} mol PTBAM, as obtained in part 2. After constant stirring under nitrogen at 80 °C for 36 h, 1.63×10^{-3} mol of (c,10) in 10 mL of DMF was added, and the reaction was allowed to continue for another 36 h. The copolymer product was isolated from DMF solution by precipitation with an excess of methanol. The collected solid was redissolved in chloroform and then precipitated with methanol.

5. Characterization of Reaction Products. The chemical structures of all the reaction products were elucidated with ^{1}H NMR (300 MHz, QE300, Nicolet) and IR spectroscopy (710B, Perkin-Elmer). The mesophase formation and glass transition were both identified with differential scanning calorimetry (DSC-4, Perkin-Elmer) and hot-stage polarizing optical microscopy (Leitz Orthoplan-Pol equipped with Mettler FP52 microthermal system). Prior to thermal analysis, each sample was heated rapidly up to and beyond the clearing point and then quenched at −320 °C/min down to −20 °C. The T_g and T_i are presented in Tables II and III were both obtained from the second heating scan at 20 °C/min.

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Registry No. Tetrabutylammonium hydroxide, 2052-49-5.

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