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Room Temperature Polyesterification

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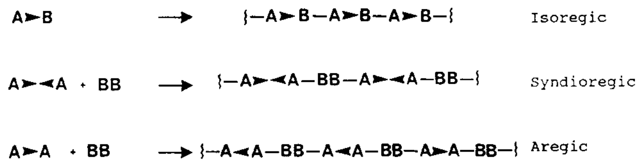
ABSTRACT: A new room temperature polymerization method has been developed for the synthesis of high molecular weight polyesters directly from carboxylic acids and phenols. The solution polymerization reaction proceeds under mild conditions, near neutral pH, and also avoids the use of preactivated acid derivatives for esterification. The reaction is useful in the preparation of isoregic ordered chains with translational polar symmetry and also in the polymerization of functionalized or chiral monomers. The conditions required for polymerization in the carbodiimide-based reaction included catalysis by the 1:1 molecular complex formed by 4-(dimethylamino)pyridine and *p*-toluenesulfonic acid. These conditions were established through studies on a model system involving esterification of *p*-toluic acid and *p*-cresol. Self-condensation of several hydroxy acid monomers by this reaction has produced routinely good yields of polyesters with molecular weights greater than 15 000. It is believed that the high extents of reaction required for significant degrees of polymerization result from suppression of the side reaction leading to *N*-acylurea. The utility of this reaction in the formation of polar chains from sensitive monomers is demonstrated here by the polycondensation of a chiral hydroxy acid.

Introduction

Polymerization by condensation reactions has several synthetic limitations which include lack of methodologies for precise control of chain length and few known reactions that take place under extremely mild conditions. This last limitation is an obstacle to synthesis of high molecular weight products from sensitive monomers that are functionalized or chiral. A related problem is the general need to convert condensation monomers to an activated derivative prior to polymerization. This precludes the direct self-condensation of "A–B" type monomers, important in the formation of isoregic polymers that have translational polar symmetry. The term isoregic is used in this manuscript to describe a form of regiochemical order, specifically that of a chain with molecular direction. This term was adapted from the definitions of Cais and Sloan[1] describing directional isomerism (regioisomerism) in vinyl polymers. As illustrated in Scheme I, condensation polymers derived from A–B monomers form chains with isoregic order. Synthetic access to this class of chain structures is only possible through this type of monomer and therefore methodologies of broad scope for its polymerization are essential. We report here on a new polymerization method, which yields high molecular weight polyesters at room temperature directly from carboxylic acids and phenols under extremely mild conditions.

Scheme I
Regiochemical Order in Condensation Polymers



Although several reactions have been developed for direct condensation of acids and amines leading to polyamides,[2] few methods currently exist to construct polyesters directly from unactivated monomers. Melt-phase transesterification has been used extensively although reaction temperatures greater than 250 °C are generally required to obtain high molecular weight polymers. The high temperatures employed prevent application of this reaction to the polymerization of monomers that contain sensitive functional groups. Also, if ester bonds preexist in the monomer, transesterification will lead to sequentially random polymer chains.[3] Recently, solution procedures for direct polyesterification have been reported by Higashi et al.[4] One of these procedures involves in situ activation of carboxylic acids with diphenyl chlorophosphate,[4a] while a second procedure employs arylsulfonyl chloride condensing agents.[4b–d] These reactions are carried out in pyridine at temperatures near 120 °C. In our experience, the method based on arylsulfonyl chloride reagents leads to undesirable phenyl tosylates as a significant side product and hence gives low molecular weight polymers. Moreover, use of milder conditions such as lower reaction temperatures gives increasing amounts of tosylate ester side products. When the mixed anhydride is allowed to form before the diphenol is introduced, good results can be obtained. This modi-

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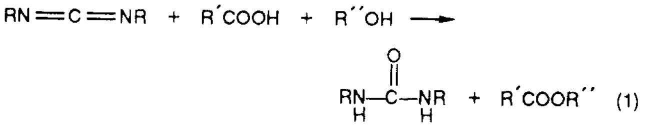
fication would not, of course, be useful for hydroxyacid monomers. The Higashi procedure also has the limitation of not being suitable for aliphatic acids and/or aliphatic alcohols.

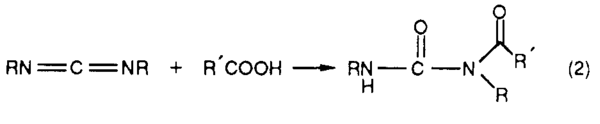
Recent advances in carbodiimide esterification[5,6] led us to explore the possible use of these reagents for direct polyesterification. As shown in eq 1, condensation occurs between equimolar mixtures of acids and alcohols driven by the addition of water across the carbodiimide groups and producing the stable urea byproduct



$$RN{=}C{=}NR + R'COOH + R''OH \longrightarrow RNH{-}\overset{\overset{\large O}{\|}}{C}{-}NHR + R'COOR'' \quad (1)$$

Since carbodiimides do not react with aliphatic alcohols or phenols except under drastic conditions,[5] one expects selective activation of the carboxylic acid, thus permitting direct esterification. Direct esterification occurs by in situ formation of activated acids, avoiding the need to prepare and handle preactivated acid derivatives such as acid chlorides. Since these derivatives are susceptible to hydrolysis by adventitious moisture present during the reaction, high conversion levels are only possible under rigorously anhydrous conditions. Such conditions are thus essential in order to obtain high molecular weight products by these conventional reactions. On the other hand, if a direct polymerization method is employed, traces of moisture can be tolerated since the activated intermediate can be regenerated should any hydrolysis occur.

Although carbodiimide chemistry has been extensively used in peptide synthesis,[7] its use in esterification chemistry has been hampered by a side reaction that converts carboxylic acids to unreactive *N*-acylureas (see eq 2). This reaction would of course preclude formation of high molecular weight products and must therefore be completely suppressed for polymerization to proceed. For example, in recent work a carbodiimide-based polyesterification was attempted but only low molecular weight products were obtained.[8] It has recently been observed that this reaction is suppressed by the use of the hyperacylation catalyst 4-(dimethylamino)pyridine (DMAP)[6a,9] and by acid catalysis.[6b,c] In this work we describe the development of a carbodiimide-based polymerization method that yields high molecular weight products.



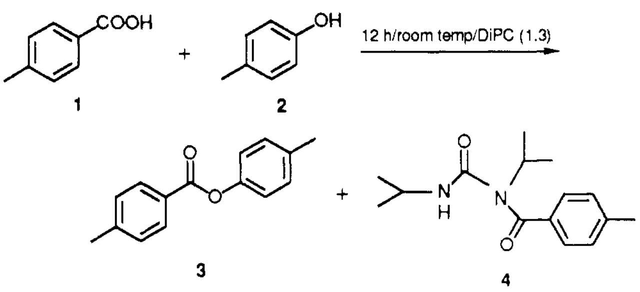
$$RN{=}C{=}NR + R'COOH \longrightarrow RNH{-}\overset{\overset{\large O}{\|}}{C}{-}N(R){-}\overset{\overset{\large O}{\|}}{C}{-}R' \quad (2)$$

Experimental Section

General Methods. All glassware was oven dried overnight at 145–155 °C. Solvents were dried by refluxing 3–5 h over an appropriate drying agent, fractionally distilled through a 10-cm Vigreux column, and stored over 4A molecular sieves. The drying agents used were phosphorous pentoxide for methylene chloride and dichloroethane, barium oxide for pyridine, and calcium hydride for benzene and dimethylformamide (DMF). *p*-Toluic acid was recrystallized from ethyl acetate, and *p*-cresol was fractionally distilled under reduced pressure. All other reagents were used as received.

^1H and ^{13}C NMR analysis were carried out at 300 and 75 MHz, respectively, on a General Electric QE300 NMR in $CDCl_3$ and referenced to TMS unless otherwise indicated. Five-second delay times and a 45° pulse width with 16K data were used for quantitative ^1H measurements. These measurements were used to characterize reaction products and also to estimate degrees of polymerization. In some cases, up to 400 transients were accumulated to improve the signal to noise ratio. Analysis of reaction products was carried out by integration of peaks assigned to known compounds. Degrees of polymerization were estimated by using end group resonances assigned by comparison to monomers and the *N*-acylurea derivative of a suitable model compound.

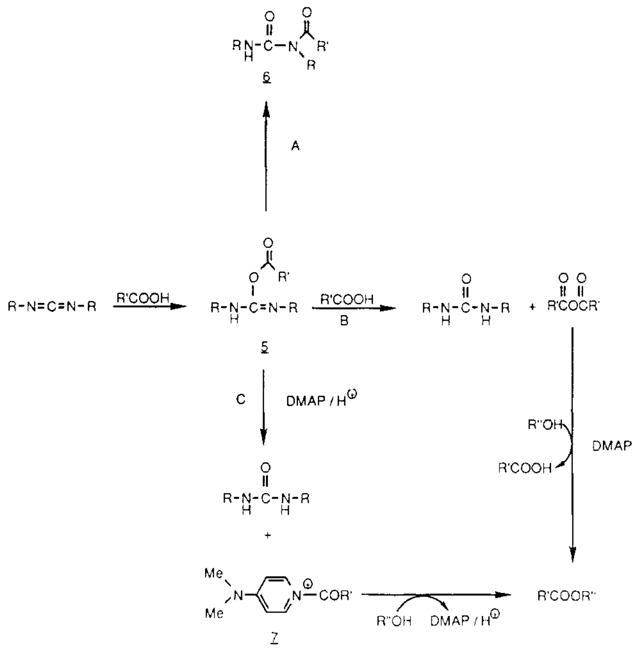
Table I



solvent	tert amine (equiv)	acid (equiv)	conv, %	3:4
CH_2Cl_2	DMAP (0.1)		91	10.5:1
CH_2Cl_2	DMAP (1.0)		94	18:1
CH_2Cl_2	DMAP (1.0)	PTSA (0.1)	95	>25:1
CH_2Cl_2	DMAP (1.0)	PTSA (1.0)	>95	>25:1
CH_2Cl_2	DMAP (1.0)	PTSA (2.0)	*a*	
CH_2Cl_2	pyridine (1.0)	PTSA (1.0)	*a*	
DMF	DMAP (1.0)	PTSA (1.0)	>95	>25:1

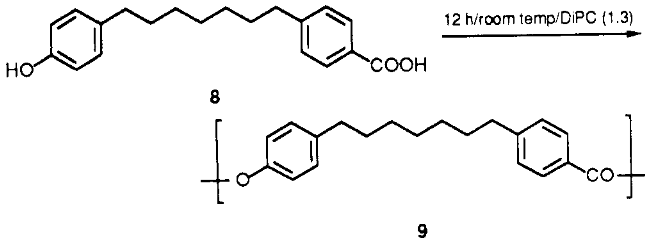
[a] Complex product mixture was obtained, which was not analyzed further.

Scheme II
Reaction Pathways in Carbodiimide Condensation



4-(Dimethylamino)pyridinium 4-Toluenesulfonate (DPTS). Hydrated *p*-toluenesulfonic acid (PTSA) is dried by azeotropic distillation of a benzene solution by using a Dean-Stark trap. An equimolar solution of DMAP in warm benzene is then added to the anhydrous benzene solution of PTSA and the two solutions are mixed thoroughly. The resulting suspension is cooled to room temperature and the solid collected by suction filtration. The crude product can be purified by recrystallization from dry dichloroethane, yielding white needles that melt at 165 °C. The reagent is not hygroscopic and is stable indefinitely when stored at room temperature.

Table II
Polycondensation of 8



solvent	reagent (equiv)	isolated yield, %	DP
pyridine	PTSA (0.2)	49	4.4
pyridine	DPTS (0.2)	70	25.1
pyridine	DPTS (2.0)	74	32.4
CH_2Cl_2	DPTS (0.2)	88	>50
CH_2Cl_2	DPTS (2.0)	83	>30
CH_2Cl_2	DMAP (2.0)	38	13.2
DMF	DPTS (2.0)	64	11.8

4-Methylphenyl 4-Toluate. A single-neck round-bottom flask was charged with 1.0 mmol of *p*-toluic acid and 1.0 mmol of *p*-cresol in 2.0 mL of dry solvent. DMAP and monohydrated PTSA were added in various amounts as shown in Table I. Diisopropylcarbodiimide (1.3 mmol) was added via syringe as a neat liquid and the entire contents were stirred 12 h at room temperature. Products were isolated by one of two methods, depending on the solvent. For those reactions conducted in pyridine or DMF, products were recovered by pouring the reaction into 20 volumes water. The solids were collected by suction filtration and dried. For those reactions carried out in methylene chloride, the solvent was removed by rotary evaporation, and the residue analyzed by ^1H NMR without further treatment.

Carbodiimide Polymerization. A single-neck round-bottom flask containing a stir bar and fitted with a Claisen adapter connected to a septum and an argon manifold was assembled hot, flame dried, and flushed thoroughly with argon. The Claisen adapter was briefly removed and replaced with a powder funnel for addition of the hydroxy acid followed by 0.1–2.0 equiv of DPTS. The Claisen adapter was replaced and the system was again flushed with argon. Dry methylene chloride (1–5 mL per 100 mg of hydroxy acid) was added via syringe and the suspension was gently warmed. If a homogeneous solution did not form once reflux temperature was reached, then a small amount of dry pyridine was added (0.1–1.0 mL per 100 mg of DPTS).[10] The solution was cooled to room temperature and diisopropylcarbodiimide (1.3–2.0 equiv) was added as a neat reagent via syringe. The number of equivalents was based on the molar quantities of carboxyl groups. Stirring at room temperature under argon was continued 12–24 h[11] and once the reaction was completed the solution was poured into 25–50 volumes of rapidly stirred methanol. At this point the solid polymer product, free from diisopropylurea, was collected.[12]

Results and Discussion

We initially explored the potential of carbodiimide polyesterification and optimized conditions through a study of the model reaction between *p*-cresol and *p*-toluic acid. In order to characterize the reaction products we synthesized the acylurea of *p*-toluic acid and analyzed its ^1H NMR spectrum.[13] Selected results from the model reaction of *p*-cresol and *p*-toluic acid are given in Table I. The reaction was carried out successfully in either methylene chloride or dimethylformamide (DMF) at room temperature by using 1.3 equiv of diisopropylcarbodiimide (DIPC). In the absence of acid catalysis, significant amounts of the *N*-acylurea 4 were obtained. However, if catalytic amounts of *p*-toluenesulfonic acid (PTSA) were added, the formation of 4 was essentially suppressed. In fact, with acid catalysis the conversion levels were high enough to be suitable for polycondensation. As shown in Table I, the optimal ratio of DMAP to PTSA was found to be nearly 1:1. If the quantity of PTSA exceeded this level, a complex mixture of products was obtained. Also, if DMAP was replaced by pyridine in an equimolar ratio of this amine to PTSA, a complex reaction mixture was also obtained.

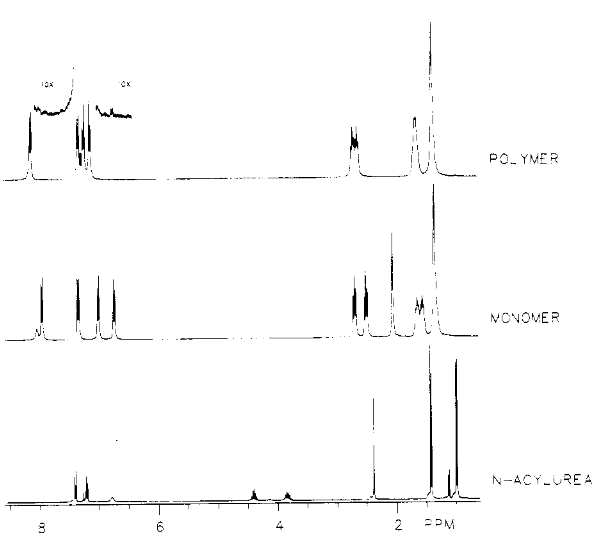


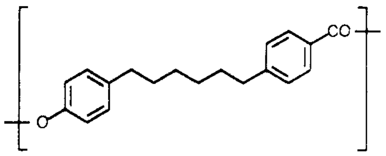
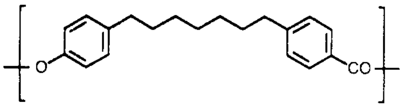
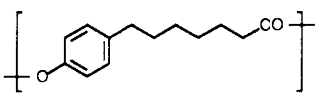
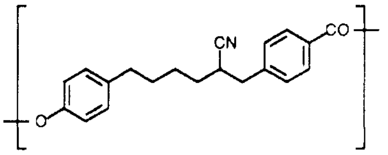
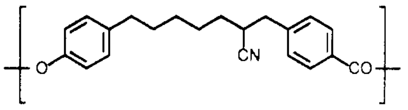
Figure 1. 300-MHz ^1H NMR spectra of polymer **9** in $CDCl_3$ (top), its corresponding monomer **8** in acetone-d_6 (center), and the *N*-acylurea prepared from *p*-toluic acid and DiPC (bottom, $CDCl_3$). The inset in the spectrum of **9** shows a 10-fold vertical expansion of the aryl protons on the phenolic and acid end groups.

The mechanism of carbodiimide condensation reactions is believed to involve the *O*-acylisourea intermediate 5 shown in Scheme II. This intermediate can follow several possible reaction pathways. Intramolecular oxygen to nitrogen acyl group transfer accounts for the formation of the *N*-acylurea (path A).[14] Bimolecular reaction between the *O*-acylisourea and a second carboxylic acid leads to the formation of the acid anhydride and urea (path B). The extent of *N*-acylurea relative to anhydride in the absence of other nucleophilic species is known to depend strongly on solvent, pK_a of the carboxylic acid, and pH of the reaction medium.[5,14] At lower pH values *N*-acylurea formation is known to be suppressed. This may account, in part, for the high conversions to ester obtained in the presence of PTSA.

The data given in Table I clearly indicate the importance of DMAP compared to pyridine. DMAP is well-known to be an outstanding catalyst for the acylation of phenols and alcohols by acid anhydrides.[9] Thus one may envision that esterification proceeds through the acid anhydride as shown in Scheme II, path B. Alternatively, it is possible to postulate that DMAP is effective at capturing the *O*-acylisourea as the active *N*-acylpyridinium intermediate 7 (Scheme II, path C). Formation of 7 from 5 involves a series of proton-transfer steps and is accompanied by the generation of urea. The importance of acid catalysis may simply be to facilitate these proton-transfer steps leading to the *N*-acylpyridinium species. Reaction of 7 with a nucleophile such as a phenol produces the ester and *N*,*N*-dimethylpyridinium, ready again for another catalytic cycle (see Scheme II).

The results described above suggested that reaction conditions could be optimized to obtain the necessary conversions for polycondensation. As previously indicated, these studies concluded that an equimolar ratio of DMAP to PTSA was optimal in terms of both conversion and suppression of *N*-acylurea formation. We therefore prepared and characterized the 1:1 molecular com-

Table III
Summary of Polyester Characterization Data

polymer	yield, %	DP	elemental anal. calcd C	calcd H	calcd N	found C	found H	found N
	88	>50	81.39	7.19	0.00	81.26	7.18	≤0.06
	88	>50	81.60	7.53	0.00	81.46	7.56	≤0.03
	60	>50	76.44	7.90	0.00	76.24	7.93	≤0.05
	93	>50	78.66	6.27	4.59	78.56	6.42	4.53
	78	>50	78.97	6.63	4.39	78.75	6.60	4.25

plex formed when DMAP and PTSA are combined. This new reagent, 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was found not to be hygroscopic and could be stored at room temperature for extended periods of time. Thus, the use of DPTS provided a convenient method to deliver the optimal 1:1 ratio of DMAP and PTSA to the reaction medium.

The studies on the model system indicated that preactivation of the acid component was not necessary in esterification by carbodiimides. For this reason we proceeded to investigate the self-condensation of the hydroxy acid monomer **8** (see Table II) synthesized in our laboratory.[15] The results obtained from reactions performed at room temperature for 12 h using 1.3 equiv DIPC are shown in Table II. This table also lists degrees of polymerization measured by ^{1}H NMR analysis of end groups. The reagent DPTS proved to be very effective for catalyzing the reaction even in amounts as low as 0.2 equiv with respect to the hydroxy acid. DMAP alone or PTSA in pyridine gave unsatisfactory results, and relative to the model system the solvent played a more critical role in the polymerization reaction. Methylene chloride was found to be the best solvent, producing high molecular weight polyesters in yields approaching 90% after purification. DMF, on the other hand, gave good results in the model system but produced significantly lower molecular weight products compared to methylene chloride.

The polymer products obtained from this mild polyesterification were found to be of remarkably high purity. Using ^{1}H NMR we have not been able to detect any *N*-acylurea terminal groups when the polymerization is performed under optimal conditions. Instead, comparable amounts of unreacted acid and phenol, presumed to be end groups, are often observed in the NMR spectrum. End-group resonances are readily identified in spectra shown in Figure 1, corresponding to polyester **9**, its corresponding monomer **8**, and the *N*-acylurea prepared from *p*-toluic acid and DiPC.[13] The inset in the spectrum of polyester **9** shows a 10-fold vertical expansion clearly revealing the aryl protons of phenolic and carboxylic acid end groups.

Table III shows elemental analysis data for several polyesters synthesized by the carbodiimide reaction. These results were obtained from products that had been simply purified by two successive precipitations of polyester solutions into methanol. The data on polymers obtained from five different monomers indicate that high-purity products are obtained from the reaction. Specifically, the nitrogen analysis reveals that urea byproduct is easily removed from the products. Furthermore, the nitrogen analysis is also consistent with a low level of terminal N-acylurea end groups, supporting the ^{1}H NMR data.

The examples in Table III provide some evidence for the general applicability of the reaction. All polyesters were prepared at room temprature in methylene chloride by using 0.5 equiv of DPTS and 1.5 equiv of DIPC. As indicated by data in Table III, molecular weights and yields are consistently high. In addition to the examples provided on esterification of aryl acids and phenols, good results have also been obtained for a monomer containing an aliphatic acid and a phenolic group (see Table III). Even though we have not yet explored the polymerization of monomers with aliphatic alcohols, the reaction has proven effective in the condensation of simple, monofunctional aliphatic alcohols with carboxylic acids.[16]

As an example to illustrate the mildness of the reaction, we present here recent data from our laboratory involving the polymerization of chiral hydroxy acid monomers.[15] We have prepared the deuterium-labeled

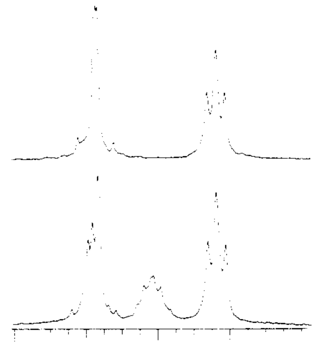
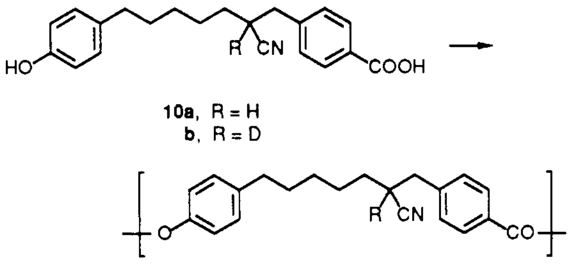


Figure 2. 300-MHz ^1H NMR spectra of polymer **11a** (bottom) and labeled polymer **11b** (top) in the region of the nitrile α-proton resonance (spectra were recorded in $CDCl_3$).

monomer **10b**[17] and polymerized it by the standard procedure as shown in eq 3. The acidity of the proton on



10a, R = H
b, R = D

11a, R = H
b, R = D

(3)

the nitrile α-carbon could result in deuterium–proton exchange under harsh reaction conditions. If deuterium–proton exchange occurs, polymerization of an enantiomerically enriched monomer would result in a polymer with lower stereochemical purity. Figure 2 shows ^1H NMR spectra of polymers **11a** and **11b** in the region of the nitrile α-carbon. These two polyesters were prepared under the standard carbodiimide conditions described above. The absence of any appreciable α-proton is clearly revealed by the spectrum of polymer **11b** in Figure 2. Integral ratios in this region for the spectrum of **11b** reveal that monomer **10b** exchanges less than 3% of its deuterium label during polymerization. Thus, this extremely mild reaction is expected to be useful in the polymerization of sensitive, optically active monomers such as **10a**.

Concentrated solutions of polymers obtained by the reaction described in this manuscript are viscous, supporting the NMR evidence for the synthesis of high molecular weight products. Also, some of the products, especially those with $(-CH_2)_7-$ spacers, form flexible solution-cast films. In subsequent publications we will report on the structure and physical properties of the polymeric materials synthesized by this new reaction.

Conclusions

We have developed a new room temperature polymerization method for the synthesis of polyesters directly from aliphatic or aryl carboxylic acids and phenols. The carbodiimide-based reaction was found to be effectively catalyzed by the 1:1 molecular complex formed between DMAP and PTSA. Polyesters having number-average molecular weights greater than 15 000 (dp > 50) have been routinely obtained in good yields and in high purity by this methodology. Since preactivated acid derivatives are not required the reaction is conveniently performed compared to other solution polyesterification methods. Furthermore, direct condensation provides a route to self-condensation of hydroxy acid monomers to form isoregic chains with polar translational symmetry. Due to the fact that the reaction is carried out at room temperature and near neutral pH, it is an extremely mild polyesterification reaction useful in the polymerization of thermally and chemically sensitive monomers.

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Registry No. **3**, 15024-08-5; **4**, 123643-10-7; **8**, 123674-21-5; **9**, 123643-20-9; **10a**, 123643-17-4; **10b**, 123643-19-6; **11a**, 123674-23-7; **11b**, 123643-23-2; DPTS, 91944-64-8; DiPC, 693-13-0; DMAP, 1122-58-3; PTSA, 104-15-4; HOC_6H_4-*p*-$(CH_2)_6C_6H_4$-*p*-CO_2H (homopolymer), 123643-12-9; HOC_6H_4-*p*-$(CH_2)_6C_6H_4$-*p*-CO_2H (SRU), 123674-22-6; HOC_6H_4-*p*-$(CH_2)_6CO_2H$ (homopolymer), 123643-13-0; HOC_6H_4-*p*-$(CH_2)_6CO_2H$ (SRU), 123643-21-0; HOC_6H_4-*p*-$(CH_2)_4CH(CN)CH_2C_6H_4$-*p*-CO_2H (homopolymer), 123643-15-2; HOC_6H_4-*p*-$(CH_2)_4CH(CN)CH_2C_6H_4$-*p*-CO_2H (SRU), 123643-22-1; *p*-toluic acid, 99-94-5; *p*-cresol, 106-44-5.

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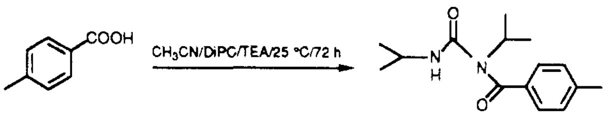
(10) In some cases it is possible to perform the polymerization of insoluble hydroxy acids without the addition of pyridine. Under these conditions, the initial suspension becomes homogeneous shortly after the addition of the carbodiimide. Since the reaction is most successful in methylene chloride without any added cosolvent, addition of pyridine should be reserved for cases in which the monomer and/or polymer are completely insoluble in methylene chloride.

(11) Diisopropylurea can often be observed as a white precipitate within the first hour of the reaction.

(12) If traces of diisopropylurea remain in the final product, the polymer can be dissolved in a suitable solvent and reprecipitated into 25–50 volumes of methanol.

(13) An authentic sample of the acylurea of *p*-toluic acid was prepared as shown below



^{1}H NMR ($CDCl_3$) δ 0.99 (d, 6 H), 1.42 (d, 6 H), 2.39 (s, 3 H), 3.84 (m, 1 H), 4.41 (m, 1 H), 6.80 (br s, 1 H), 7.21 (d, 2 H), 7.41 (d, 2 H); ^{13}C NMR ($CDCl_3$) δ 20.87 (q), 21.40 (q), 22.26 (q), 42.61 (d), 50.35 (d), 126.49 (d), 129.17 (d), 134.2 (s), 141.01 (s), 154.25 (s), 172.63 (s). MS EI (70 eV), *m/z* (relative intensity) 262 (9%, M^+), 176 (14), 162 (20), 119 (100), 91 (28), 58 (20).

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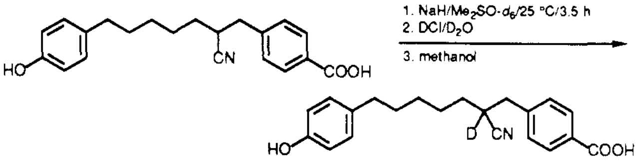
(17) Deuterium labeling was achieved as shown below



Deuterium coupling in the ^{13}C NMR specified the isotopic site at the nitrile α-position. The percent deuterium incorporated was determined to be 94.3% by field ionization mass spectrometry and NMR measurements. ^{1}H NMR δ (Me_2SO-d_6) 1.30 (M, 2 H), 1.53 (m, 6 H), 2.44 (t, 2 H), 2.93 (ABq, 2 H), 6.65 (d, 2 H), 6.95 (d, 2 H), 7.41 (d, 2 H), 7.90 (d, 2 H), 9.10 (s, 1 H), 12.91 (br s, 1 H). ^{13}C NMR (acetone-d_6) δ 27.45 (t), 29.12 (t), 32.17 (t), 32.30 (t), 33.49 (t, C(D)CN, *J*(CD) = 20.6 Hz), 35.31 (t), 38.42 (t), 115.75 (d), 122.11 (s), 129.95 (d), 130.07 (d), 130.59 (d), 133.90 (s), 144.08 (s), 156.05 (s), 167.50 (s).

Thermal Aging of Tetraalkyl Ammonium Doped Polyacetylenes

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ABSTRACT: The stability of tetraalkyl ammonium doped polyacetylenes was examined under accelerated conditions by monitoring the evolution of their intrinsic properties by utilizing electrical conductivity, DSC, and ESR measurements. A first-order rate equation was deduced from the electrical measurements, which leads to an apparent activation energy of about 28 kcal/mol for the counterions studied. A simple mechanism for this inherent instability, which stems from the protonation of the doped sites by the tetraalkyl ammonium ions, was suggested and was verified by elemental analysis and IR spectral studies of the degraded films and also by the gas chromotographic analysis of the degradation products. An ion-exchange method was devised to surpass the 7% doping level attainable by the direct reduction with the R_4N^+ ion doping agents. The behavior of reduced β-carotene, considered to be the soluble analogue of the insoluble PA, toward its R_4N^+ counterion was investigated, and a similar proton abstraction mechanism was put forward to explain its reactivity. In all cases, the order of reactivities of the carbanions were rationalized on the basis of their redox potentials.

Introduction

Developments in the field of conducting polymers have been retarded due to their extreme sensitivity to ambient atmospheric conditions. Both the parent conjugated system and its doped form (oxidized or reduced) are subject to losing their inherent interesting properties. The deterioration of the properties of the doped form may be attributed to extrinsic or intrinsic factors. The extrinsic instability of the doped polyacetylene (PA), taken as the prototype of conducting polymers, arises from the reactivity of the polycarbanion or polycarbenium ion toward moisture or other reactive species. On the other hand, the intrinsic stability of the system is controlled by the reaction between the dopant ion and the polymer backbone and hence is dopant dependent. Investigations on the p-doped PA have revealed that the iodine-oxidized films are relatively less stable than that obtained from AsF_5.[1] Similar studies by Pochan et al.[2] and by Druy et al.[3] have demonstrated that iodine- and perchlorate-doped samples lose their conductivity quite rapidly under vacuum, due to the reaction of the polymer backbone with the counterion. Yang et al.[4] also observed the instability of these doped polymers and pointed out that the reaction of PA with perchlorate counterions can be explosive.

In contrast, alkali-metal-doped PA exhibits intrinsic stability and leads to a dopant cation-dependent conductivity enhancement during thermal annealing.[5] While realizing the electrochemical insertion of R_4N^+ ions into PA, MacDiarmid et al.[6] have remarked on the degradation of the properties of the PA electrode. We have accomplished a similar insertion of organic cations by a purely chemical method, by developing a complex carbanionic dopant system that functions by a guest cation insertion mechanism.[7] The classical insertion technique becomes irrelevant in this case due to the extreme reactivity of the carbanions with the R_4N^+ counterions. This reactivity is governed by the basicity of the carbanions, which can be correlated with their redox potentials. It then becomes interesting to examine how a polycarbanion, existing as a highly delocalized system but confined to the solid state, interacts with its countercation. We have undertaken a detailed study of the kinetics and mechanism of the degradation of the R_4N^+-doped PA. In order to better define the reactivity of a reduced polyenic sys-

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