Synthesis of Aramid Copolymers from *N,N'*-Aroylbis(lactams)

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ABSTRACT: The melt polymerization of *N,N'*-isophthaloylbis(2-pyrrolidone), *N,N'*-isophthaloylbis(valerolactam), or *N,N'*-isophthaloylbis(caprolactam) with 1,3-phenylenediamine or 3,4'-diaminodiphenyl ether provides high molecular weight aramid copolymers containing Nylon 4, 5, or 6 components, showing that the diamine condensation occurs at both the aroyl and the lactam carbonyls. The in situ generated lactams act as plasticizers during the preparation and processing of the copolymers and can be extracted with methanol. The effects of impurities such as carboxyl groups in the bis(lactams) and of the lactam ring size on the copolymer compositions and their molecular weights are described. Structure–property relationships in the copolymers are discussed.

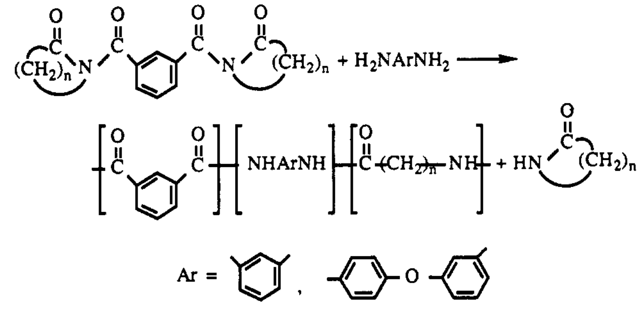
Introduction

Melt condensation, the preferred commercial procedure, is not suitable for the synthesis of aramids from aromatic diamines and aromatic dibasic acids because of the low reactivity of the diamines and the decomposition of the polymers prior to melting.[1] Instead, aramids are normally prepared by use of aromatic acid dichlorides and processed from solutions that often contain large amounts of inorganic salts. Typical examples are those of the commerical aramids such as poly(1,3-phenyleneisophthalamide),[2] poly(1,4-phenyleneterephthalamide),[3,4] and a copoly(terephthalamide) from 1,4-phenylenediamine and 3,4'-diaminodiphenyl ether.[5] A worthwhile objective has been to prepare salt-free aramids or aramid copolymers by a melt process. Such polymers would have the high glass transition temperature, T_g, and good thermal stability of aramids and, at the same time, have the advantage of melt processibility.

In this paper, we have explored the *N,N'*-aroylbis(lactam) route to make high molecular weight polymers in the plasticized melt phase. Specifically, the polymerizations of *N,N'*-isophthaloylbis(lactams) with 1,3-phenylenediamine (MPD) and 3,4'-diaminodiphenyl ether (3,4'-DDE) are described (see Scheme I). 3,4'-DDE was found to be quite unique in that its polymers never phased out from their melts under a variety of conditions. This made it possible to better understand the factors that influence the molecular weights and composition of such copolymers. The results of other aromatic diamines will be reported in a separate publication.

Polymerization of *N,N'*-aroylbis(lactams) with aromatic diamines to make aramid copolymers has been reported in the literature.[6,7] Corresponding AB type aramid copolymers have been made from *N*-(4-aminobenzoyl)-lactams.[8–10] The main aim of these syntheses, like ours, was the preparation of melt-processible aramid copolymers due to plasticization by the in situ generated lactams. However, only very low inherent viscosity polymers were obtained presumably due to their phasing out (vide infra) from the melt. Thus, the Japanese patent application[6] describes the condensation of *N,N'*-isophthaloyl- and *N,N'*-terephthaloylbis(lactams) with aromatic diamines to polymers with reduced viscosities <0.5, although significantly higher viscosity values of polymers were obtained via solid phase polymerization in vacuum. The Russian workers[7] polymerized *N,N'*-isophthaloylbis(caprolactam) with 1,3-phenylenediamine at 250 °C to obtain a polymer having a reduced viscosity of only 0.37.

Scheme I



Experimental Section

Analytical Methods. The inherent viscosities (η_{inh}) of the polymers were determined at 25 °C on solutions containing 0.5 g of polymer in 100 mL of *N,N'*-dimethylacetamide containing 4% LiCl by weight.

Glass transition temperatures (T_g) and crystalline melting points (T_m) of the copolymers were determined by differential scanning calorimetry (DSC) with a Du Pont 2100 Thermal Analyzer. Melting points and purity of the bis(lactams) were also measured by DSC.[11]

^{1}H NMR spectra of the lactam-free copolymers were recorded on dimethyl-d_6 sulfoxide solutions with either a Varian Unity-400 spectrometer or a Nicolet NT-300 spectrometer equipped with Fourier transform accessories. The ^{13}C NMR spectra were recorded with a Varian Gemini-200 spectrometer operated at 50.3 MHz with a time-shared deuterium lock on DMSO-d_6 using Waltz-16 proton decoupling during signal acquisition. A delay time of $5T_1$ was used to ensure quantitative results.

Synthesis of *N,N'*-Isophthaloylbis(lactams). *N,N'*-Isophthaloylbis(2-pyrrolidone),[6,12] *N,N'*-isophthaloylbis(valerolactam),[6] and *N,N'*-isophthaloylbis(caprolactam)[6] are known. They were prepared by reacting isophthaloyl chloride with the respective lactams in the presence of triethylamine in toluene using a modified workup procedure to improve product yield and purity. The following general procedure was used: A dry 3-L, three-neck Morton flask was equipped with mechanical stirrer, reflux condenser, and addition funnel, was purged with N_2, and charged with 1.5 mol of freshly distilled lactam, 152 g (1.5 mol) of triethylamine, and 750 mL of toluene. The mixture at ambient temperature, but 0 °C in the case of *N,N'*-isophthaloylbis(2-pyrrolidone), was stirred, and a solution of 152 g (0.75 mol) of isophthaloyl chloride in 250 mL of toluene in the addition funnel was added dropwise over a period of 1 h. The reaction mixture became warm and a white precipitate separated. The mixture then was heated to reflux for 15 min, during which time much

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Table I
MPD-I/6 Copolymers[a]

item	amt of COOH in IBC,[b] mequiv/kg	comments	η_{inh}, dL/g	amt of Nylon 6 units, mol %: from ^{1}H NMR (eq 2)	amt of Nylon 6 units, mol %: total from ^{13}C NMR (eq 3)	amt of Nylon 6 units, mol %: aliph–NHCO–aliph from ^{13}C NMR (eq 4)	DSC data: T_g, °C	DSC data: T_m, °C
1	4.6	solid separated	0.78	30.3	30.5	2.1	211.1	390
2	15.6	solid separated	0.66	31.3	32.0	2.2	210.9	388
3	21.3	no solid separated	0.78				210.7	no endotherm
4	35.8	no solid separated	0.63	32.3	33.4	3.2	210.2	no endotherm
5	47.9	solid separated	0.58	33.3	34.6	3.3	204.8	382
6	91.2	solid separated	0.49	35.4	35.8	3.2	200.2	380

[a] Polymerizations were carried out at 280 °C. [b] *N,N'*-Isophthaloylbis(caprolactam).

Table II
3,4'-DDE-I/4 Copolymers[a]

item	amt of COOH in IBP,[b] mequiv/kg	η_{inh}, dL/g	amt of Nylon 4 units, mol %: from ^{1}H NMR (eq 2)	amt of Nylon 4 units, mol %: total from ^{13}C NMR (eq 3)	amt of Nylon 4 units, mol %: aliph–NHCO–aliph from ^{13}C NMR	T_g, °C
1	5.1	0.53	38.4	36.3	none	185.3
2	11.8	0.30	31.6	30.2	none	183.2
3	31.7	0.51	22.0	20.3	none	208.9
4	53.0	0.51	24.7	23.1	none	209.8
5	61.5	0.48	23.7	21.0	none	208.2
6	120.0	0.47	18.8	19.9	none	211.3

[a] Polymerizations were carried out at 220 °C for 1.5 h. [b] *N,N'*-Isophthaloylbis(2-pyrrolidone).

Table III
3,4'-DDE-I/5 Copolymers[a]

item	amt of COOH in IBV,[b] mequiv/kg	η_{inh}, dL/g	amt of Nylon 5 units, mol % (eq 2)	amt of aramid linkages, mol % (eq 5)	T_g, °C
1	1.0	0.93	7.4	92.0	234.0
2	2.7	0.69[c]	8.9	91.0	227.1
3	14.9	0.70	12.2	87.0	225.1
4	33.2	0.67	13.3	85.7	221.7
5	47.5	0.47	15.7	83.0	220.6
6	72.5	0.54	16.4	82.1	218.5

[a] Polymerizations were carried out at 250 °C for 1.5 h during stirring. [b] *N,N'*-Isophthaloylbis(valerolactam). [c] Not stirred.

Table IV
3,4'-DDE-I/6 Copolymers[a]

item	amt of COOH in IBC,[b] mequiv/kg	η_{inh}, dL/g	amt of Nylon 6 units, mol %: from ^{1}H NMR (eq 2)	amt of Nylon 6 units, mol %: total from ^{13}C NMR (eq 3)	amt of Nylon 6 units, mol %: aliph–NHCO–aliph from ^{13}C NMR (eq 4)	T_g, °C
1	0.56	0.96	16.3	16.8	2.0	218.6
2	1.2	1.10[c]	17.4	18.6	3.5	219.9
3	7.3	0.89	23.1	21.8	0.0	207.4
4	31.7	0.77	26.2	25.5	0.0	205.7
5	52.7	0.73	29.7	30.0	3.0	198.1
6	108.0	0.46	35.2	39.6	7.5	174.1

[a] Polymerizations were carried out at 250 °C for 1.5 h during stirring. [b] *N,N'*-Isophthaloylbis(caprolactam). [c] Reaction time 4 h.

of the precipitate dissolved. The products crystallized upon cooling to room temperature were collected. The slurry and the filter cake were rinsed with sufficient toluene to wet the entire cake. The triethylammonium chloride was removed by agitating the solid with 1 L of deionized water and collecting the solid product by filtration. Repeating this process three times sufficed to remove all the water-soluble impurities. The product was dried in a vacuum oven at 80 °C under a sweep of N_2. The bis(lactams) thus obtained were analyzed for carboxyl impurities by a titration method described in the literature.[13] These were formed presumably by partial hydrolysis of isophthaloyl chloride groups. To reduce the carboxyl impurity, the bis(lactams) were extracted with dilute aqueous sodium carbonate solution, with methanol or with ethanol. This treatment decreased the carboxyl level to less than 30 mequiv/kg, and increased the product purity to 99.0 ± 0.5% (DSC). Further purification of the bis(lactams), usually necessary for making higher inherent viscosity polymers, was effected by recrystallization.

The yield of *N,N'*-isophthaloylbis(2-pyrrolidone) was 179 g (79.6%) with a carboxyl content of 93 mequiv/kg. Methanol washing decreased the carboxyl level to 4.8 mequiv/kg, and recrystallization from acetonitrile/methanol further reduced the carboxyl content to only 2 mequiv/kg. Its DSC revealed two sharp melting points at 157.8 and 161.7 °C, which may be attributed to two crystalline forms.

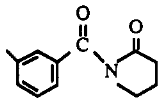
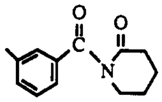
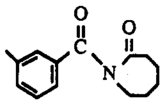
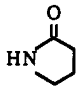
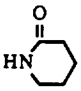
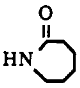
The yield of *N,N'*-isophthaloylbis(valerolactam) was 227 g (92.0%) with 9.3 mequiv/kg of carboxyls. Recrystallization from methyl ethyl ketone reduced the carboxyl content to 1 mequiv/kg, and its purity was judged to be 99.94% by DSC; the mp was 164.4 °C.

The yield of *N,N'*-isophthaloylbis(caprolactam) was 86.8% and it analyzed for 6.7 mequiv/kg of carboxyls. After recrystallization from THF it had <1 mequiv/kg of carboxyl content, and its purity by DSC was 99.99%; the mp was 141.4 °C.

N,N'-Isophthaloylbis(3-methylvalerolactam) was prepared by essentially the same procedure as the other bis(lactams), except that the reaction was scaled down one-third and the workup procedure was different. After the addition of the isophthaloyl chloride solution was complete, the reaction mixture was stirred for 3 h and then filtered. A small amount of solid, presumably triethylammonium chloride, was collected. The filtrate was stripped of toluene by vacuum distillation leaving a pasty yellow solid. This was stirred with 200 mL of ethanol for 30 min and filtered. A white solid was collected, washed with 100 mL of ethanol, and then dried in a vacuum oven at 80 °C for 3 h to yield 49 g of product (55%), mp 122.5 °C. The ^{1}H NMR spectrum ($CDCl_3$) showed absorptions with the following chemical shifts (from an internal reference of TMS): δ 7.74–7.32 (4 H, aromatic), 3.80 (2 $N-CH_2$), 2.63 and 2.20–1.83 (4 CH_2), 1.64 and 1.60 (2 CH), 1.23 and 1.22 (2 CH_3). These data are consistent with the structure of *N,N'*-isophthaloylbis(3-methylvalerolactam). The product had 3.0 mequiv/kg of carboxyl groups and was used for polymerization without further purification.

Polymerization. A typical polymerization was carried out as follows: A mixture of 0.02 mol of *N,N'*-isophthaloylbis(lactam) and 0.02 mol of the aromatic diamine in a glass reactor was thoroughly purged by an alternating N_2/vacuum cycle. Then, while under N_2, the mixture was heated with a Wood's metal bath at 220–280 °C. As the mixture melted, the reactor was shaken gently to mix the reactants. The polymerization usually was carried out for 90 min and then cooled to room temperature to obtain a clear amber-colored polymer, which was ground and

Table V
Infrared and ^{13}C NMR Data of *N,N'*-Isophthaloylbis(lactams) and Monomeric Lactams

bis(lactam) or lactam	IR $\nu_{C=O}$, cm^{-1} lactam	IR $\nu_{C=O}$, cm^{-1} aroyl	^{13}C NMR $\delta_{C=O}$, ppm lactam	^{13}C NMR $\delta_{C=O}$, ppm aroyl
	1738 and a shoulder toward high frequency[a]	1666, 1653[a]	174.162	169.133
	1706	1675	173.237	172.933
	1701	1679	176.972	172.755
	1693 (1700)[b]		179.354	
	1671 (1677)[b]		172.599	
	1662 (1675)[b]		179.351	

[a] Two absorptions due to two crystalline structures. [b] Values in parentheses are from: Conley, Robert T. *Infrared Spectroscopy*; Allyn and Bacon, Inc.: Boston, 1972; p 152.

extracted three times with 200 mL of boiling methanol. A white polymer was isolated which was dried in a vacuum oven at 80 °C under a sweep of N_2. Its inherent viscosity, ^1H NMR, and DSC were then determined.

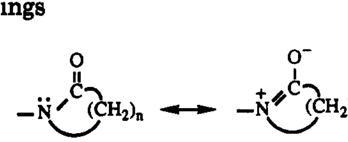
Stirring of the polymerization mixture was found to have little or no effect on the polymer molecular weight. Partial removal of the free lactams at reduced pressure usually gave higher inherents and less aliphatic component in the copolymers.

Results and Discussion

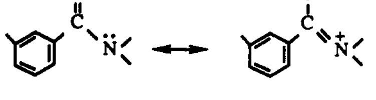
It was originally thought that the melt polymerization of *N,N'*-isophthaloylbis(lactams) with aromatic diamines at 250–300 °C gave pure aramids.[6] However, later work showed that the lactam ring opened as well to give aramid–Nylon copolymers.[7] Furthermore, model studies by Stehlicek and Sebenda[14,15] pointed out that at these high temperatures the copolymer composition could not be used to determine the relative rate of attack of an aromatic amine on the exo vs endocyclic carbonyls because of competing side reactions, such as transamidation of the copolymers with free lactam, which scramble the kinetic products.

In our work, we tried to separate to some extent the kinetic and thermodynamic effects on copolymer composition. We carried out the polymerizations at 220–280 °C and isolated the aramid copolymers from the lactam-plasticized melts. Tables I–IV list the pertinent data of various copolymers. Although the final compositions of the copolymers are determined by their thermodynamic equilibration with free lactam, carboxyl impurities in the bis(lactams) have a profound effect on composition and molecular weight. For example, during the polymerization of *N,N'*-isophthaloylbis(caprolactam) with 1,3-phenylenediamine, the copolymer would phase out[16] of the plasticized melt when the bis(lactam) had either too high or too low a carboxyl content (see Table I), indicating the high sensitivity of the polymerization to carboxyl ends. This precluded further consideration of the MPD-I/6 compositions because the inhomogeneity in the plasticized melts would prevent the equilibration of free lactam and semicrystalline copolymer. High amounts of carboxyl impurities may be the reason why previous workers did not get MPD-I/6 copolymer of high inherent viscosity.[6,7]

The thermodynamic equilibrium between the copolymer and the free lactam should depend on the lactam ring strain. Infrared spectroscopy has been used to determine the relative ring strains of lactams.[17,18] Table V lists the carbonyl stretching frequencies of both the *N,N'*-isophthaloylbis(lactams) and the corresponding free lactams. The lactam $\nu_{C=O}$ increases in the order of five- > six- > seven-membered lactams because the internal ring strain for the five-membered lactam decreases the carbonyl angle (N—CO—C) from the 120° of regular sp^2 hybridization. This increases the s character of the σ bond of the carbonyl, which results in its higher stretching frequency.[19] Furthermore, the five-membered lactam has less tendency to accommodate sp^2 hybridization at the carbonyl carbon than do the six- and seven-membered lactams because of the same angle strain. Therefore, the resonance of the nitrogen lone pair with the lactam carbonyl should be much less in the five-membered ring than in the six- and seven-membered rings



which itself would also lower the carbonyl stretching frequencies of the valerolactam and caprolactam.[20] The nitrogen lone pair of *N,N'*-isophthaloylbis(2-pyrrolidone) would then be more free to interact with the aroyl carbonyl[21]



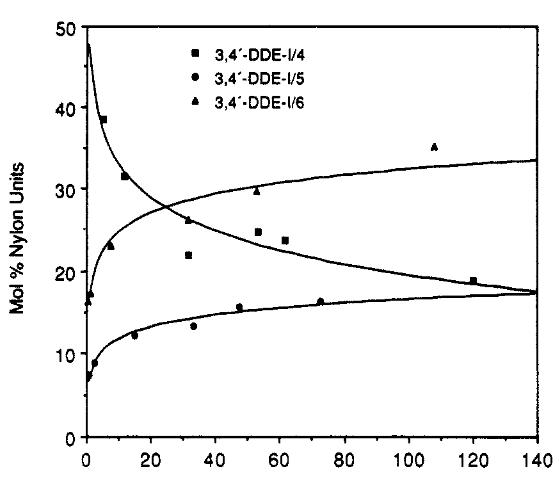
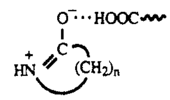


Figure 1. Effect of carboxyl impurities and the lactam ring size on the Nylon content.

This is consistent with the lower stretching frequencies of the aroyl carbonyls in *N,N'*-isophthaloylbis(2-pyrrolidone) (1666, 1653 cm^{-1}) vs those of the bis(valerolactam) (1675 cm^{-1}) and bis(caprolactam) (1679 cm^{-1}), respectively. The ^{13}C NMR data (Table V) provide further support for this rationale. For example, the lone pair resonance of an amide group usually lowers the chemical shift of the carbonyl carbon.[22] The chemical shift of the aroyl carbon of *N,N'*-isophthaloylbis(2-pyrrolidone) is lower than those of the bis(valerolactam) and bis(caprolactam).

The resulting perturbations of the carbonyls by the lactam ring strains lead to kinetic effects in the initial condensation of the aromatic diamines with the bis(lactams). Consequently, *N,N'*-isophthaloylbis(2-pyrrolidone) reacts more readily at the lactam carbonyl rather than at the aroyl carbonyl. This is seen quite clearly in Figure 1 for the lowest carboxyl content, where the tendency of the 2-pyrrolidone ring to open gives the highest level of aliphatic content in its copolymer. However, the opposite was seen in the case of *N,N'*-isophthaloylbis(valerolactam) or *N,N'*-isophthaloylbis(caprolactam), where the diamine attack occurred preferentially at the aroyl carbonyl. Nevertheless, these are kinetic effects that can ultimately be masked by the thermodynamic equilibration of the copolymers with the free lactams.

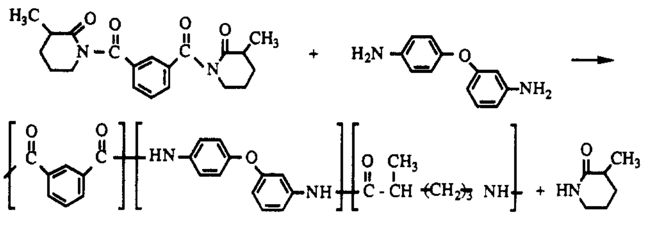
The ring opening polymerization of lactams has been studied quite extensively.[23-25] The carboxyl-catalyzed, amine-propagated ring-opening polymerization of caprolactam is especially well known.[26-28] Presumably, the carboxyl groups protonate the caprolactam ($n = 5$) carbonyl



thus making the ring more prone to attack by an amine. On the other hand, valerolactam ($n = 4$) opens much less readily because it is inherently more stable than caprolactam.[20] The ring-opening polymerization of 2-pyrrolidone ($n = 3$) probably cannot be carboxyl-catalyzed on the basis of the ring strain analysis because association of the carboxyl proton with the lactam carbonyl would be retarded due to a low contribution of the necessary resonance structures. This is quite consistent with the fact that Nylon 4 is formed only under very basic conditions.[29,30] However, the thermodynamic equilibration of the copolymers with the free lactams is readily established, as is shown by the leveling off of the curves in Figure 1, especially in the presence of higher levels of carboxyls. This is due to the well-known acid-catalyzed transamidation involving the reaction of the polymer amine ends with the amide groups.[31,32] It may be noted that the crossing of the 3,4'-DDE-I/6 curve over that of 3,4'-DDE-I/4 indicates that 2-pyrrolidone is more stable than caprolactam under these conditions.

When the competing kinetic and thermodynamic effects of both lactam ring strain and carboxyl catalysis upon the initial condensation and the subsequent equilibration via transamidation are considered, it is clear why the highest molecular weight copolymers with the lowest aliphatic contents are obtained from *N,N'*-isophthaloylbis(valerolactam) and *N,N'*-isophthaloylbis(caprolactam) having the least amount of carboxyl impurities. The low aliphatic content of these copolymers is maintained either by stopping the polymerization before reaching equilibrium or by removing some free lactam in vacuo.

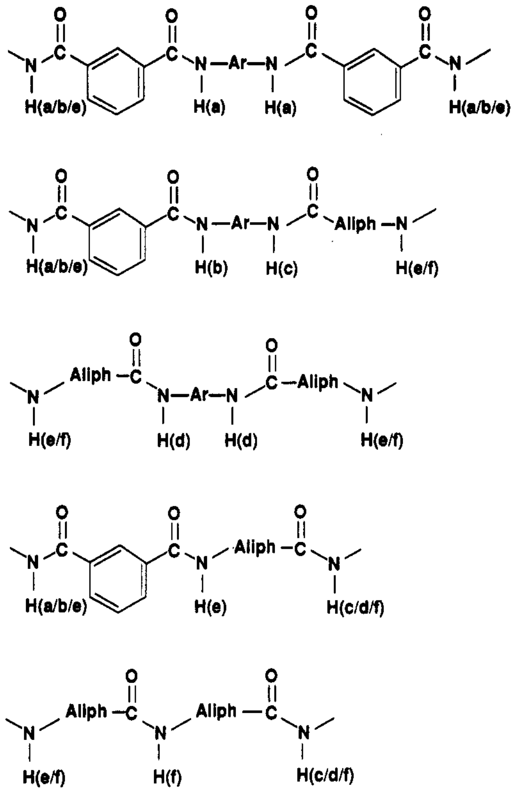
Methyl Substituent on Valerolactam. The effect of a methyl substituent on the polymerizability of caprolactam has been extensively reported.[33-35] In general, methyl substitution decreases the polymerizability of caprolactam primarily due to conformational effects which favor cyclization over the opening of the lactam ring. We employed this approach to make an aramid copolymer with the least amount of aliphatic component. Specifically, *N,N'*-isophthaloylbis(3-methylvalerolactam) containing 3 mequiv/kg of carboxyl groups was polymerized with 3,4'-DDE at 250 °C.



The 3,4'-DDE-I/3Me5 copolymer had an inherent viscosity of 0.7. Its aliphatic content was indeed lower at 5.4 mol % (1.9 wt %) vs 8.9 mol % (3.2 wt %) for the comparable unsubstituted copolymer (item 2, Table III). However, its T_g was 221 °C vs 227 °C for the 3,4'-DDE-I/5 copolymer, showing the effect of methyl substitution on the polymer chain mobility. For comparison, the 3,4'-DDE-I homopolymer displays a T_g of 240 °C.[36]

Determination of the Copolymer Composition. The relative amounts of aliphatic and aromatic components in the copolymers were determined from their ^{1}H and ^{13}C NMR spectra by integrating the areas under the NH proton and the amide carbonyl absorptions. This enabled a more precise understanding of the copolymer microstructure than was possible with simple integration of the aliphatic and aromatic regions of the spectra. The assignments of the different NH protons (see Table VI) and carbonyls to specific polymer sequences was made from a study of model compounds. All the NH absorptions are observable except for those that are due to the aliph–NHCO–aliph groups, which are completely obscured by the aromatic protons in this region. Figure 2 shows the ^{1}H NMR spectrum of the aromatic region of a typical 3,4'-DDE-I/6 copolymer and the assignments of the different NH groups. The corresponding absorptions in the other copolymers are approximately in the same regions. In retrospect, accurate integration of the aromatic protons is precluded due to interference from the NH protons that lie in the same region.

Table VI
^{1}H NMR Chemical Shifts of the Amide Hydrogens in the 3,4′-DDE-I/5 and 3,4′-DDE-I/6 Copolymers



N-H	δ_H, ppm	N-H	δ_H, ppm
a	10.51, 10.49 (doublet)	d	9.97
b	10.46	e	8.42, 8.39 (doublet)
c	9.99	f	~7.7

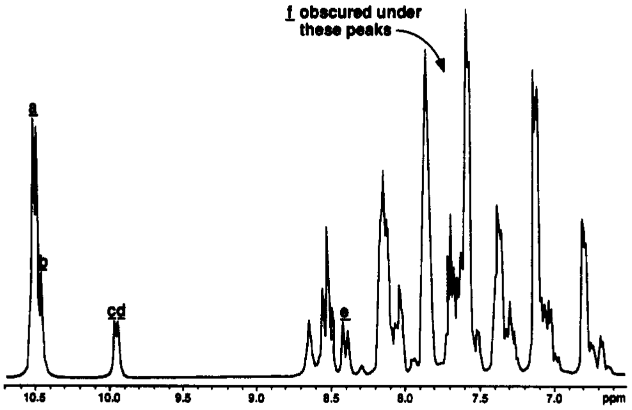


Figure 2. 400-MHz ^{1}H NMR spectra of 3,4′-DDE-I/6 copolymers.

The aliphatic content of the copolymers can then be calculated as follows:

$$\text{mol \% of Nylon units} = 100\frac{e+f}{a+b+c+d+e+f} \qquad (1)$$

The polymer sequences of Table VI show that c + d = e, so for polymers where the concentration of aliph–NHCO–aliph approaches zero (f → 0, vide infra), eq 1 simplifies to

$$\text{mol \% of Nylon units} = \frac{100}{\left[1+\frac{1}{2}\left(1+\frac{a+b}{c+d}\right)\right]} \qquad (2)$$

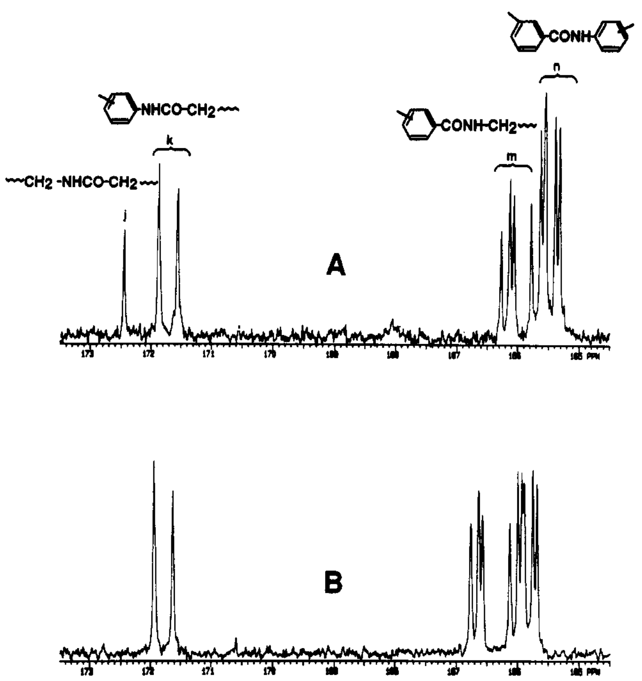


Figure 3. ^{13}C NMR spectra of 3,4′-DDE-I/6 (A) and 3,4′-DDE-I/4 (B) copolymers.

In the ^{13}C NMR spectra, only the copolymers containing the Nylon 6 units, MPD-I/6 (Table I) and 3,4′-DDE-I/6 (Table IV), showed the presence of the aliph–NHCO–aliph groups. For example, Figure 3 shows the spectrum of the 3,4′-DDE-I/6 copolymer with the absorption of the aliph–NHCO–aliph carbonyl at 172.5 ppm (j). Absorptions due to the other amide carbonyls are indicated by k, m, and n. The 3,4′-DDE-I/4 copolymers, although having relatively high aliphatic content, e.g., item 1 in Table II, showed no carbonyl absorption corresponding to the aliph–NHCO–aliph (Figure 3). Likewise, the 3,4′-DDE-I/5 copolymers showed no detectable level of such group. The total aliphatic content and the concentration the aliph–NHCO–aliph group can be calculated from eqs 3 and 4, respectively. Tables I, II, and IV list the aliphatic contents

$$\text{mol \% of Nylon units} = 100\frac{j}{j+k+\frac{m+n}{2}} \qquad (3)$$

$$\text{mol \% of aliph–NHCO–aliph groups} = 100\frac{j+k}{j+k+\frac{m+n}{2}} \qquad (4)$$

of the copolymers calculated from their ^{1}H and ^{13}C NMR spectra. For the 3,4′-DDE-I/5 copolymers, only the values calculated from their ^{1}H NMR spectra are given in Table III.

The formation of the aliph–NHCO–aliph groups in the caprolactam-based copolymers occurs most probably by first formation of $-CO-(CH_2)_5-NH_2$ end groups via the amide interchange reaction. The aliphatic amine group can then react with the *N*-aroyl caprolactam end groups, with the Ar–NHCO–($-CH_2)_5-$ units, or with the free caprolactam itself. However, the rate of cyclization of $-NHCO-(CH_2)_n-NH_2$ is much faster when $n = 3$ or 4; consequently, no aliph–NHCO–aliph groups are formed in their respective copolymers.

An aramid is defined as a long-chain synthetic polyamide having at least 85% of its amide linkages (–NHCO–) attached to two aromatic rings.[37] The amount of such

Table VII
Number Average Molecular Weight of Copolymers

copolymer	Nylon content mol %	Nylon content wt %	η_{inh}, dL/g	$\bar{M}_n$
3,4′-DDE-I/5	8.5	2.7	1.02	33 800
	7.9	2.5	0.99	33 200
	7.6	2.4	0.74	17 900
	8.8	2.8	0.52	15 157
3,4′-DDE-I/6	25.1	10.3	1.07	32 200
	24.7	10.1	0.97	28 000
	23.7	9.6	0.75	18 400
	24.7	10.1	0.63	18 700

linkages in these copolymers can be calculated from the following equation:

$$\text{mol \% of aramid linkages} = \frac{100}{\left[1 + \dfrac{2(c+d)}{a+b}\right]} \qquad (5)$$

According to this criterion, only copolymers made from *N,N*′-isophthaloylbis(valerolactam) (see Table III) and *N,N*′-isophthaloylbis(3-methylvalerolactam) can be classified as aramids. The copolymers made from the corresponding bis(caprolactam) and bis(2-pyrrolidone) have too much aliphatic content to qualify as aramids.

Molecular Weight Determination. The number average molecular weight (M_n) of some representative samples of 3,4′-DDE-I/5 and 3,4′-DDE-I/6 copolymers were determined by membrane osmometry (MO) for correlation with their inherent viscosities (Table VII). The consistency of the viscosity data was confirmed by repetitive analysis, so that any error can be attributed to the molecular weight data. Clearly, the polymers with inherent viscosities of 0.7–1.0 have relatively high molecular weights ranging from 18 000 to 33 000. Although there is some scatter in the M_n data, they can be fitted to an empirical equation

$$\eta_{\text{inh}} = 4.4 \times 10^{-4} M_n^{0.75}$$

with a standard error estimate of ±11%. While not a rigorous application of the Mark–Houwink–Sakurada equation,[38] this correlation puts these polymers in the category of well-solvated random coil polymers, and is useful in estimating the M_n for samples based on their inherent viscosities.

Polymers with inherent viscosities as high as 1.3 have been prepared for the 3,4′-DDE-I/5 and 3,4′-DDE-I/6 copolymers in the plasticized melt, especially when vacuum distillation of a portion of the lactams is employed during the polymerization, although not specifically in the case of the latter. From the above relationship, such polymers would have M_n values on the order of 45 000, which demonstrates the efficacy of this condensation polymerization to generate very high molecular weights.

Polymer Structure. The MPD-I/6 copolymers that separated from the melt during polymerization showed melting point endotherms, T_m, in their DSC (see Table I) before decomposition. The copolymers that did not phase out (items 3 and 4) showed no melting points, which indicates that they had no crystallinity. None of the 3,4′-DDE-I/5 and 3,4′-DDE-I/6 copolymers had melting points, and their X-ray diffraction patterns showed only an amorphous halo. The 3,4′-DDE-I homopolymer is amorphous as well due to a lack of symmetry in 3,4′-DDE.[36] This leads to a quasi-copolymer effect because 3,4′-DDE allows for random sequencing of meta and para catenation in its position in the polymer chain.

Conclusions. A method for making high molecular weight aramid copolymers via the melt polymerization of *N,N*′-isophthaloylbis(lactams) with selected aromatic diamines has been demonstrated. Copolymers are isolated by washing out free lactams generated in situ during polymerization. Specifically, *N,N*′-isophthaloylbis(valerolactam) and *N,N*′-isophthaloylbis(caprolactam) have been condensed with 3,4′-diaminodiphenyl ether at 250 °C to give 3,4′-DDE-I/5 and 3,4′-DDE-I/6, respectively, having M_n values in the range 18 000–45 000. Their Nylon 5 and 6 contents are in the ranges 7–12 and 15–35 mol %, respectively. They are completely amorphous by X-ray. However, they have relatively high T_g's ranging from 200 to 235 °C, thus making them suitable for high-temperature applications such as composite matrices, adhesives, and coatings.

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References and Notes

(1) Morgan, P. W. *Condensation Polymers*; Interscience Publishers: New York, 1963; pp 190–192.

(2) (a) Morgan, P. W. *Macromolecules* **1977**, *10*, 1381. (b) Sweeny, W. U.S. Pat. 3,287,324, 1966.

(3) (a) Kwolek, S. L.; Morgan, P. W.; Schaefgen, J. R.; Gulrich, L. W. *Macromolecules* **1977**, *10*, 1390. (b) Kwolek, S. L.; Morgan, P. W.; Sorensen, W. R. U.S. Patent 3,063,966, 1962. (c) Bair, T. I.; Morgan, P. W.; Killian, F. L. *Macromolecules* **1977**, *10*, 1396. (d) Bair, T. I.; Morgan, P. W. U.S. Pat. 3,673,143, 1972; U.S. Pat. 3,817,941, 1974.

(4) (a) Vollbracht, L. In *Comprehensive Polymer Science*; Allen, G., Bevington, J. C., Eds.; Pergamon Press: Oxford, U.K., 1989; Vol. 5, pp 375–386. (b) Vollbracht, L.; Veerman, T. J. U.S. Pat. 4,308,374, 1981.

(5) (a) Ozawa, S. *Polym. J.* **1987**, *19*, 119–125. (b) Ozawa, S.; Nakagawa, Y.; Matsuda, K.; Nishihara, T.; Yunoki, H. U.S. Pat. 4,075,172, 1978.

(6) Miwa, S.; Kuze, K. Jpn. Pat. 19714, 1970; *Chem. Abstr.* **1970**, *73*, 99408f.

(7) Korshak, V. V.; Frunze, T. M.; Kurashev, V. V.; Danilevskaya, L. B.; Volkova, T. V. *Vysokomol. Soedin.* **1975**, *A17*, 1409.

(8) Spiewak, J. W. U.S. Pat. 3,869,431, 1975.

(9) Akkapeddi, M. K.; Housny, A.; Walsh, M. S. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **1986**, *27*, 120–121.

(10) Mathias, L. J.; Moore, D. R.; Smith, C. A. *J. Polym. Sci., Polym. Chem. Ed.* **1987**, *25*, 2699.

(11) Hunter, J. E.; Blaine, R. L. In *Purity Determinations by Thermal Methods*; Blaine, R. L., Schoff, C. K., Ed.; ASTM Special Technical Publication 838; ASTM: Philadelphia, 1983; pp 29–38.

(12) Ogata, N.; Sanui, K.; Konishi, K. *Konbunshi Kagaku* **1973**, *30*, 202; *Chem. Abstr.* **1973**, *79*, 79227s.

(13) Taylor, G. B.; Waltz, J. E. *Anal. Chem.* **1947**, *19*, 448.

(14) Stehlicek, J.; Sebenda, J. *Collect. Czech. Chem. Commun.* **1980**, *45*, 2524.

(15) Stehlicek, J.; Sebenda, J. *Collect. Czech. Chem. Commun.* **1981**, *46*, 1458.

(16) The "phasing out" is actually crystallization of the polymer. Spherulites can be distinctly seen in the melt that is not clear. Crystallization limits the polymer molecular weight buildup.

(17) Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Wiley: New York, 1958; pp 213–214.

(18) Hall, H. K., Jr.; Zbinden, R. *J. Am. Chem. Soc.* **1958**, *80*, 6428.

(19) Bartlett, P. D.; Stiles, J. *J. Am. Chem. Soc.* **1955**, *77*, 2806.

(20) The carbonyl stretching frequency is slightly lower for caprolactam than valerolactam, which could be because the seven-membered ring relieves its strain via the incipient N— bond. Molecular models show that shortening the N— bond decreases the seven-membered ring strain, as well as the torsional interactions between vicinal C—H bonds.

(21) This might explain why the exocyclic aminolysis of *N*-benzoyl-2-pyrrolidone with aliphatic diamines is much slower than that of the corresponding valerolactam and caprolactam derivatives.[14]

(22) Stothers, J. B. *Carbon-13 NMR Spectroscopy*; Academic Press: New York, 1972; p 289.

(23) Sebenda, J. In *Comprehensive Chemical Kinetics*; Bamford, C. H., Tipper, C. F. H., Eds.; Elsevier Scientific Publishing Co.: New York, 1976; pp 379–471.

(24) Koshak, V. V.; Frunze, T. M. *Synthetic Heterochain Polyamides*; Daniel Davey & Co.: New York, 1964.
(25) Hall, H. K., Jr. *J. Am. Chem. Soc.* **1958**, *80*, 6404.
(26) Kruissink, C. A.; van der Want, G. M.; Staverman, A. J. *J. Polym. Sci.* **1958**, *30*, 67.
(27) Heikens, D.; Hermans, P. H.; van der Want, G. M. *J. Polym. Sci.* **1960**, *44*, 437.
(28) Korshak, V. V.; Kudryavtsev, R. V.; Sergeev, V. A.; Intsikson, L. B. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1962**, 1378.
(29) Ney, W. O., Jr.; Crowther, M. U.S. Pat. 2,739,959, 1956.
(30) Wynn, R. W.; Glickman, S. A.; Chiddix, M. E. *Macromolecular Synthesis*; Wiley: New York, 1972; Vol. 3, p 106.
(31) Beste, L. F.; Houtz, R. C. *J. Polym. Sci.* **1952**, *8*, 395.
(32) Miller, I. K. *J. Polym. Sci.* **1976**, *14*, 1403.
(33) Schaeffler, A.; Ziegenbein, W. *Chem. Ber.* **1955**, *88*, 1374.
(34) Wolinski, L. E.; Mighton, H. R. *J. Polym. Sci.* **1961**, *49*, 217.
(35) (a) Cefelin, P.; Doskocilova, D.; Frydrychova, A.; Sebenda, J. *Collect. Czech. Chem. Commun.* **1964**, *29*, 485. (b) Cefelin, P.; Frydrychova, A.; Schmidt, P.; Sebenda, J. *Collect. Czech. Chem. Commun.* **1967**, *32*, 1006. (c) Cefelin, P.; Frydrychova, A.; Labsky, J.; Schmidt, P.; Sebenda, J. *Collect. Czech. Chem. Commun.* **1967**, *32*, 2787.
(36) Imai, Y.; Kajiyama, M.; Ogata, S.-I.; Kakimoto, M. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 3183.
(37) *FTC Code of Federal Regulations*; The National Archives of the United States: Washington, DC, 1986; Vol. 16, p 62.
(38) Flory, P. J. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca, NY, 1953; pp 310–312.