Polymers with Cycloaliphatic Units in the Chain

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ABSTRACT

This paper describes the synthesis and characterization of some polycondensation polymers (poly- and copolyamides, polyesters) which contain cycloaliphatic units in their chains. Syntheses were carried out by a low-temperature polycondensation technique (interfacial and solution), and also by the Yamazaki method in NMP-pyridine solution using triphenylphosphite as the catalyst. The products obtained were characterized by elemental analysis, IR, and x-ray diffraction. Thermoanalytical data have shown very good thermal properties for all products, but especially for the aromatic cycloaliphatic polyamides which were stable up to 400°C.

INTRODUCTION

Aromatic polyamides and polyesters are an important class of processable heat-resistant polymers. They combine excellent mechanical properties with good thermal stability and high melting temperatures [1, 2]. Although this last property is a virtue in many applications, it may create problems in processing especially when melting points are around or exceed the chemical decomposition temperature. This has prompted vigorous research activities on the modification of such polymer structures in order to preserve the desirable characteristics while overcoming the processing difficulties.
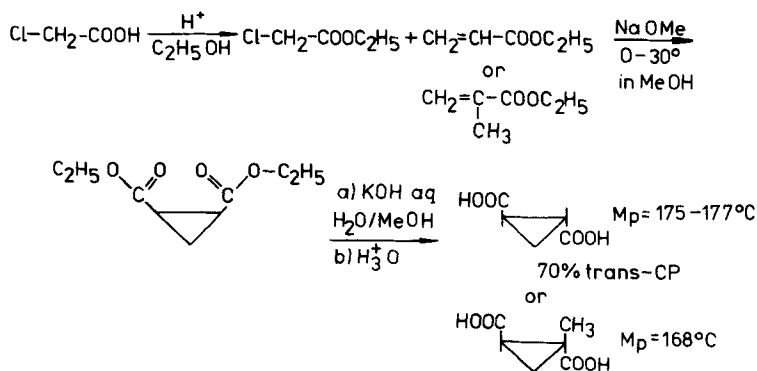
In the last few years we have undertaken a program to synthesize various polyamides and polyesters with cycloaliphatic units in the main chain with the hope of obtaining products close to the usual aramides and arylates. We also hoped to achieve new properties such as photoreactivity, photodegradability, and functionalization possibilities by opening up the cycloaliphatic ring [3, 4].

There are a number of articles in the literature that discuss the synthesis of polymers with cycloaliphatic units in the main chain, but they are principally concerned with the synthesis of such polymers by cycloolefin polymerization [5] or cyclophotoaddition of bisolefinic derivatives [6]. Only a few works contain information on polycondensation polymers, although the subject has been intensively studied in many laboratories [7].

Thus, in this paper we dwell on approaches to the synthesis and behavior of some condensation polymers of various structures (poly- and copolyamides, polyesters) where, with the usual monomers of an aliphatic or aromatic nature nearby, the cycloaliphatic units were inserted. We have worked mainly with racemic trans-isomers of cyclopropane- and 1-methylcyclopropane-1,2-dicarboxylic and cyclobutane-1,2-dicarboxylic acids.

EXPERIMENTAL

The cyclopropane dicarboxylic acids were prepared according to the following scheme [8]:

$$Cl-CH_2-COOH \xrightarrow[C_2H_5OH]{H^+} Cl-CH_2-COOC_2H_5 + CH_2=CH-COOC_2H_5 \xrightarrow[0-30°]{NaOMe}$$

$$\text{or} \quad \text{in MeOH}$$

$$CH_2=\underset{CH_3}{\overset{|}{C}}-COOC_2H_5$$

a) KOH aq
H_2O/MeOH

b) H_3^+O

$M_p = 175-177°C$

70% trans-CP

or

$M_p = 168°C$

The isolation of isomers was done by recrystallization from acetonitrile, and the cycloaliphatic structure of the acids obtained was checked by elemental analysis, IR, and ^{1}H-NMR spectroscopy (Fig. 1) [9].

The trans-1,2-cyclobutane dicarboxylic acid was supplied by Merck. Acid chlorides of the monomers employed were prepared by standard
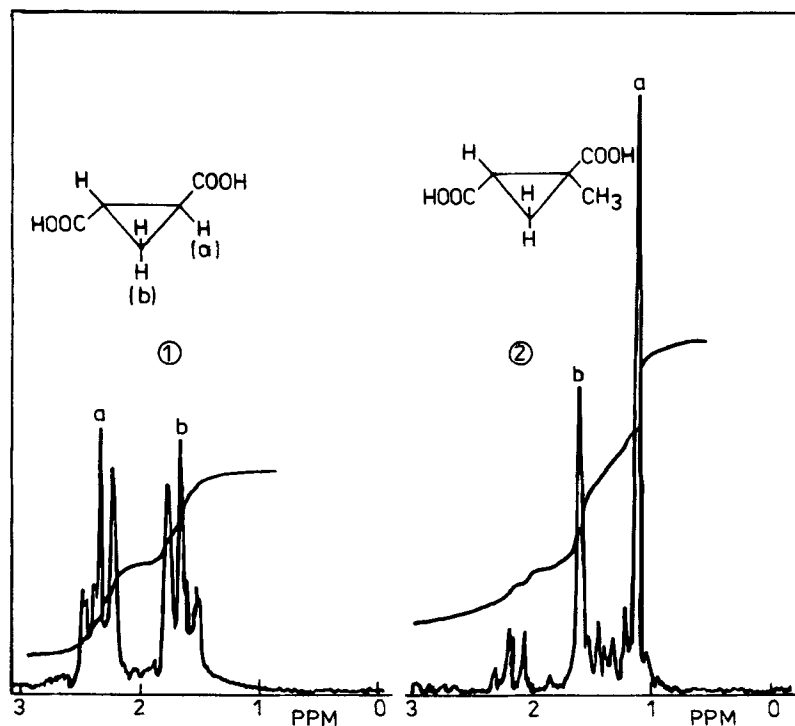
FIG. 1. ^{1}H-NMR spectra of cyclopropane-trans-1,2-dicarboxylic acid (1) and 1-methylcyclopropane-trans-1,2-dicarboxylic acid (2).

methods and purified by fractional distillation or recrystallization (terephthaloyl chloride).

The synthesis of polymers was carried out by low-temperature interfacial and solution polycondensation in a manner described elsewhere [10] by using various organic solvents.

Polymer characterization was done by elemental analysis, IR measurements performed on a SPECORD-IR-71 apparatus in KBr pellets, thermal analysis on a PAULIK-PAULIK-ERDEY MOM Budapest apparatus, and by x-ray diffraction on a Kristalloflex-4-Siemens diffractometer with a 2°/min registration speed. Viscosity measurements were performed with an Ubbelohde viscometer in suitable solvents for the polymers studied.

RESULTS AND DISCUSSION

By employing cycloaliphatic derivatives for obtaining the polymers, a careful selection of synthetic methods is necessary. Under strong

reaction conditions, equilibrium between trans- and cis-isomers may occur. In addition, by using highly rigid monomer units, the rate of reaction of their derivatives is expected to be considerably lower than for the corresponding derivatives of flexible monomer units. Therefore, well-characterized reactions which are fast enough, efficient, and proceed under mild conditions have to be considered. One of these is the Schotten-Baumann reaction of diacid chlorides with diamines or diols. Consequently, polymers were synthesized by low temperature condensation (interfacial or/and solution) from various aromatic diamines and cycloaliphatic-dicarbonylchlorides:
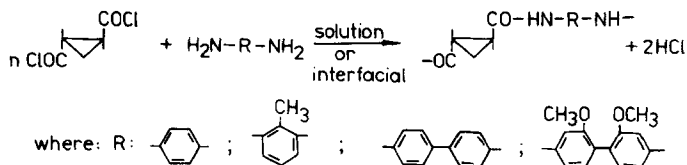
In order to obtain aromatic-cycloaliphatic polyamides by interfacial polycondensation, the diamines were dissolved in an acetone/water (6:4 v/v) mixture.

The reaction promoted by triphenyl phosphite and pyridine has been also employed for the direct polycondensation of dicarboxylic acids and aromatic diamines following the reaction [11, 12]
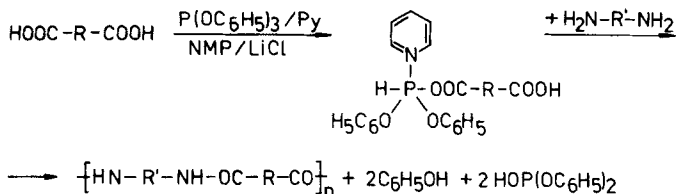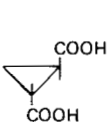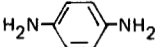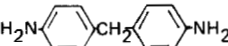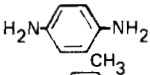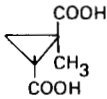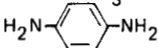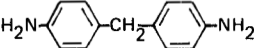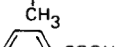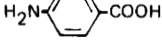

In this way, high yields and moderately high molecular weight polymers were obtained (Table 1).

Reactions were carried out at 100°C for 2 h in a solution containing LiCl (4% w/v) initially dissolved in NMP in the presence of various amounts of pyridine (Py). The best results were obtained for the ratio NMP/Py = 5:1 (v/v). The use of N,N-dimethylacetamide (DMAA) did not give significant changes of molecular weight and polymer yield. It is worth mentioning that polycondensation results in poorer yield when substituted monomers are employed.

From the IR spectra of the synthesized polymers, some characteristic absorptions like those at 1620-1650 cm^{-1} for amide I or 1530 and 1590 cm^{-1} for amide II structures can be outlined. It is interesting that products obtained by interfacial polycondensation (Fig. 2) outline better amide III structures (1250-1300 cm^{-1}) while those prepared by

TABLE 1. Aromatic-Cycloaliphatic Polyamides Obtained in NMP-Py Solution Containing LiCl (time = 2 h, T = 100 °C)

Dicarboxylic acid	Diamine	Yield, %	η_{inh} [a]
cyclopropane-1,2-dicarboxylic acid (COOH, COOH)	H₂N—C₆H₄—NH₂	100	0.35
	H₂N—C₆H₄—CH₂—C₆H₄—NH₂	97.1	0.23
	H₂N—C₆H₃(CH₃)—NH₂	98.7	0.3
1-methylcyclopropane-1,2-dicarboxylic acid (COOH, CH₃, COOH)	H₂N—C₆H₄—NH₂	79.0	0.25
	H₂N—C₆H₄—CH₂—C₆H₄—NH₂	80.2	0.22
	H₂N—C₆H₃(CH₃)—NH₂	67.5	0.18
	H₂N—C₆H₄—COOH	100	0.67

[a]Concentrations 0.5 g/dL in H_2SO_4 at 30°C, $P(OC_6H_5)_3$ = 10 mmol, NMP = 50 mL, Py = 10 mL.

the low-temperature solution method (Fig. 3) reveal the amide I ($1600-1690$ cm^{-1}) and amide II (1550 cm^{-1}) structures.

X-ray investigations of several polyamides have shown that these products may occur in three crystallographic modifications: α, β, and γ, which refer to triclinic, monoclinic, and hexagonal systems, respectively. It was established, for instance, that polycaproamide usually occurs under α and β modifications, while the polydodecaneamide crystallizes only in the γ-form without a $\gamma \rightarrow \alpha$ transition [12]. The x-ray diffraction patterns of the aromatic cycloaliphatic polyamides outline a good similarity between the monoclinic modification of polyamide-6 and the image obtained from poly(p-phenylendiamine-trans-cyclopropanedicarbox)amide, poly-p-FDA-t-CP. The shape and position of the maxima may be interpreted as being the same crystallographic system. It is obvious that this polymer retains a high degree of crystallinity.

For the other polyamides (Fig. 4) it is difficult to make an assignment of the reflections obtained; it might be that higher dimensions of the diamines used increases the distance between the diffraction planes and, consequently, polyamides will pertain to other crystallographic systems.

Among the synthesized polyamides, the poly(p-FDA-t-CP) and poly(benzidine-t-CP) might be of interest due to their chain rigidity,
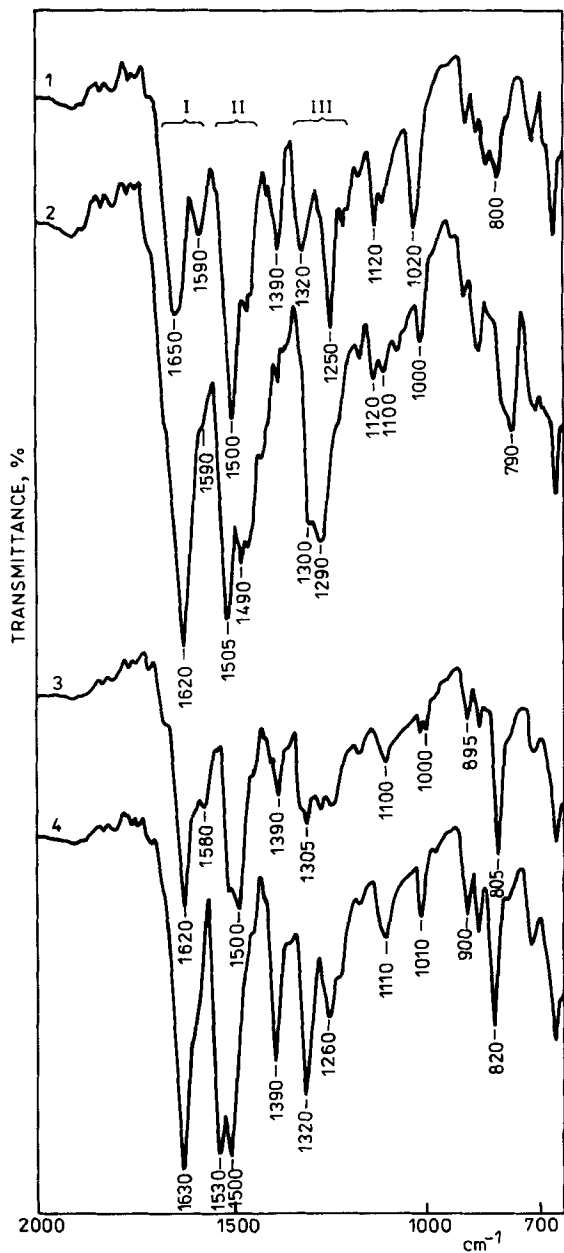
FIG. 2. IR spectra of the aromatic cycloaliphatic polyamides obtained by the interfacial polycondensation technique. (1) Poly(3,3'-dimethoxybenzidine-trans-CPC)amide; (2) poly(2,6-diaminotoluene-trans-CPC)amide; (3) poly(benzidine-trans-CPC)amide; (4) poly(p-FDA-trans-CPC)amide.
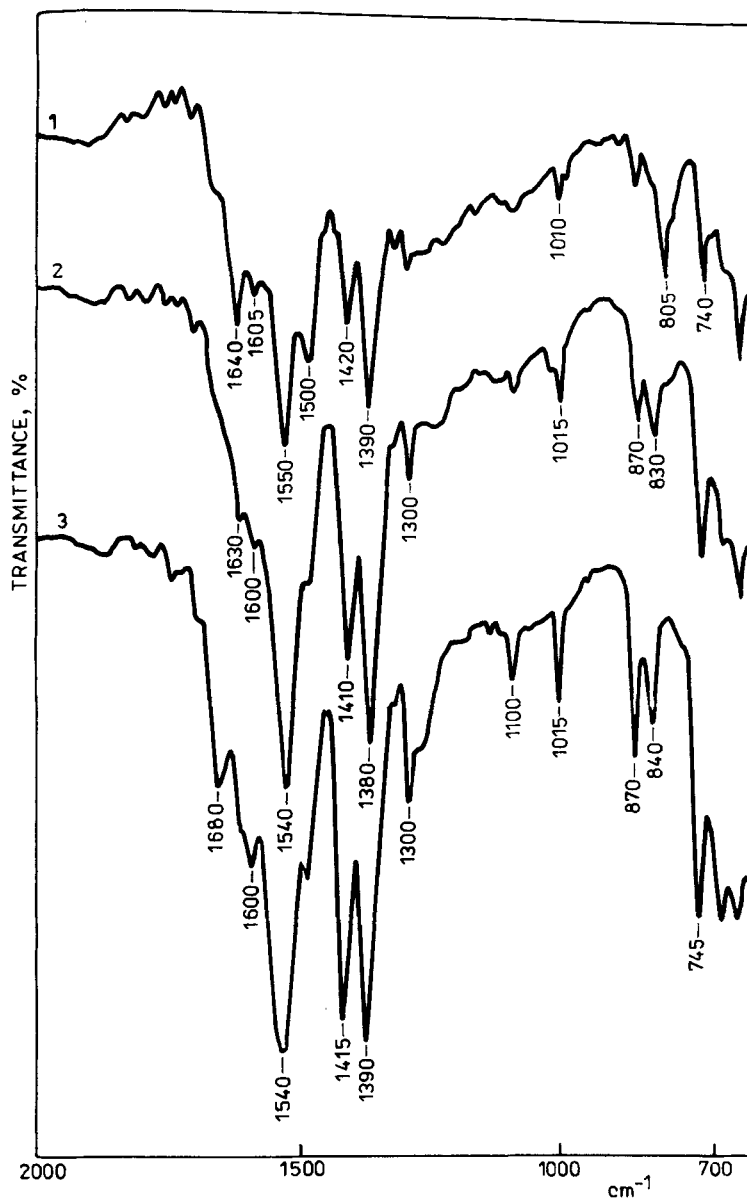
FIG. 3. IR spectra of the aromatic cycloaliphatic polyamides ob-
tained by the solution polycondensation technique. (1) Poly(benzidine-
trans-CPC)amide; (2) poly(3,3'-dimethoxybenzidine-trans-CPC)amide;
(3) poly(2,6-diaminotoluene-trans-CPC)amide.
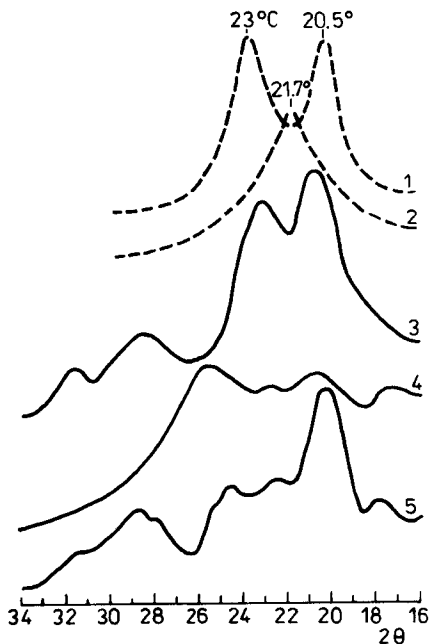
FIG. 4. X-ray diffraction patterns for aromatic cycloaliphatic polyamides. (1) Nylon 6 (α, β); (2) nylon 6 (hexagonal); (3) poly(p-FDA trans-CPC)amide; (4) poly(3,3'-dimethoxybenzidine-trans-CPC)amide; (5) poly(benzidine-trans-CPC)amide.

FIG. 5. Ln τ-ln $\dot{\gamma}$ dependence for poly(p-FDA-trans-CPC)amide 2% solution in concentrated H_2SO_4.

which may form ordered structures in solution. Rheoviscosimetric measurements made at various temperatures on a 2% poly(p-FDA-t-CP)-H_2SO_4 solution (Fig. 5) showed a low activation energy, which may be interpreted as showing that in such conditions there are no associations of macromolecular chains. In spite of that, η_{red}-c plots display deviation from a straight line. Further studies are in progress on this topic.

Random Copolyamides

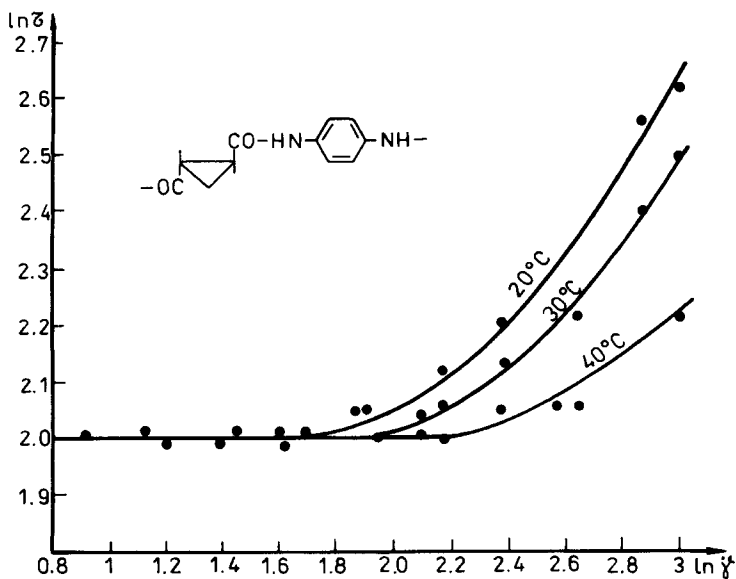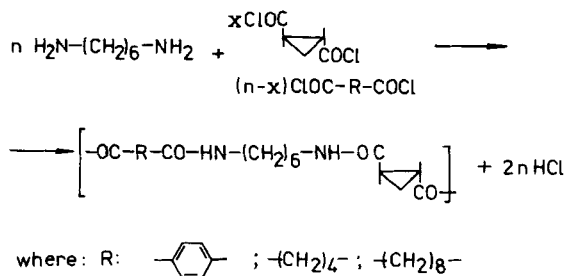Random copolyamides were prepared according to the following scheme by the interfacial polycondensation technique:

$$n \ H_2N-(CH_2)_6-NH_2 \ + \ \begin{array}{c} x\,ClOC \\ \diagdown_{COCl} \end{array}$$

$$(n-x)ClOC-R-COCl \longrightarrow$$

$$\longrightarrow \left[-OC-R-CO-HN-(CH_2)_6-NH-OC\diagdown_{CO}\right] + 2n\,HCl$$

$$\text{where: R:} \quad -\!\!\langle\bigcirc\rangle\!\!- \ ; \ -(CH_2)_4- \ ; \ -(CH_2)_8-$$

The structural characteristics of these copolymers, obtained from their IR spectra, are in good agreement with the proposed compositions. Cyclopropane units in the macromolecular chains are indicated by 930 cm^{-1} stretching vibrations. Also to be noted are the adsorptions which belong to various amide structures: 1625–1640 cm^{-1} (amide I), 1530–1550 cm^{-1} (amide II), and a shoulder at 1290–1300 cm^{-1} (amide III). These assignments are in good agreement with x-ray diffraction data [9].

The properties of random copolyamides are frequently checked through their melting behavior. Figure 6 diagrams depict melting temperatures for the synthesized copolyamides. It is obvious that for poly-(hexamethylene-adipyl-co-trans-1,2-cyclopropanedicarboxamide) a drop of the melting point appears for an equimolecular ratio of the two diacids. This may be explained by changes of the fusion enthalpy (ΔH_u) and entropy (ΔS_u). ΔH_u reflects the intermolecular interactions in the polymer. Thus, due to the insertion of cyclopropane units (5–30%), whose dimensions differ from that of adipyl units, the structural order in the former nylon 66 is disturbed:
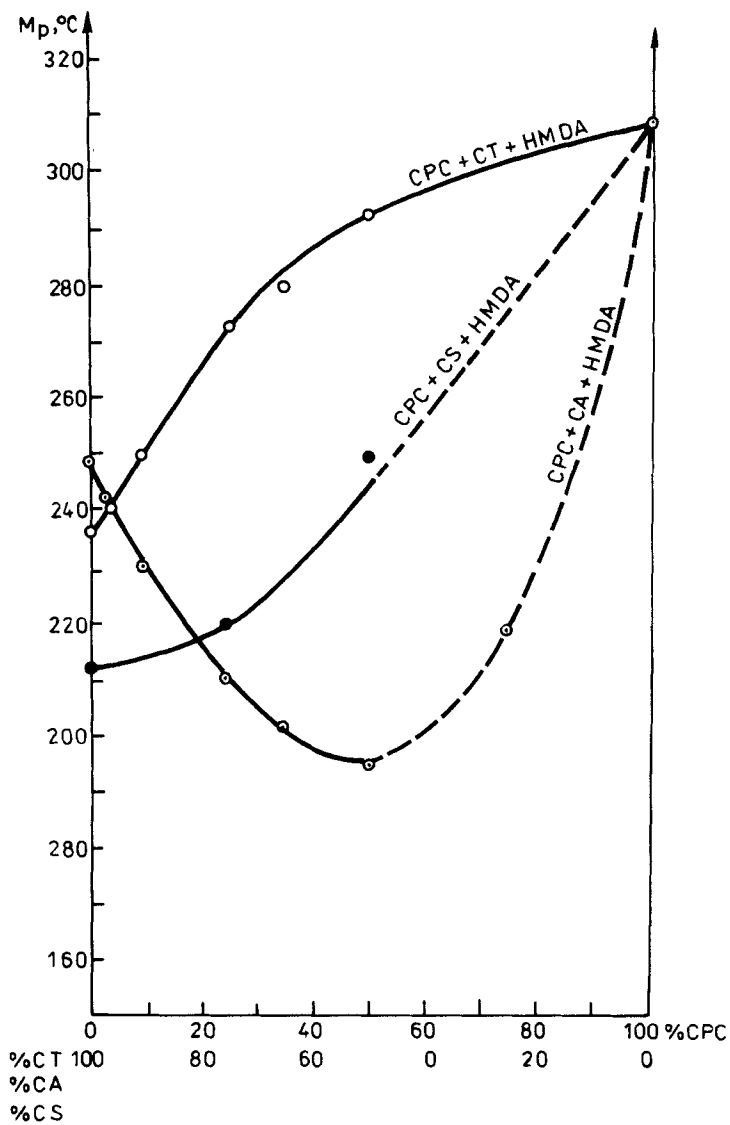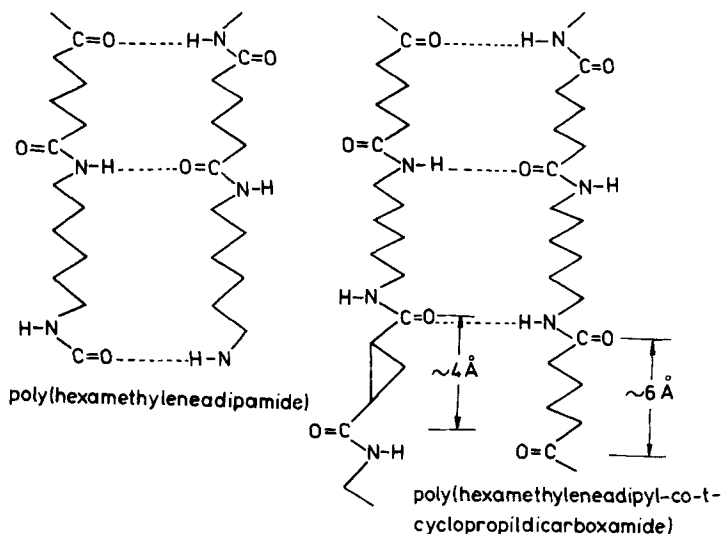
FIG. 6. Melting temperature diagram for random copolyamides.

poly(hexamethyleneadipamide)

poly(hexamethyleneadipyl-co-t-
cyclopropildicarboxamide)

As a consequence, the frequency of hydrogen bonds and ΔH_u decrease, while chain flexibility and ΔS_u increase. With over 50% of cycloaliphatic units, the macromolecular chains display a pronounced rigidity and the melting temperature rises again.

A different behavior is displayed by the other two copolyamides. The substitution of the aromatic ring by cyclopropane in poly(hexamethylene terephthalamide) results in an isomorphic polymer with increased rigidity and a higher melting point. This should account for cycloaliphatic derivatives behaving like aromatic ones.

Nylon 610 modified with cyclopropane-1,2-dicarboxylic acid displays an almost similar behavior as the previous polymer. The influence of the cycloaliphatic unit appears at a content of more than 30% and results in a continuous increase of the melting temperature (it lowers chain flexibility).

Aromatic Cycloaliphatic Polyesters

Synthesis of aromatic cycloaliphatic polyesters was carried out by the interfacial polycondensation technique. Among the aromatic diols used, the most promising results were obtained with bisphenol A (Table 2) which condensed in higher yields and to higher molecular weight products [10].

The polymers bore a resemblance to the structure of the corresponding substrates. This was confirmed by IR and ^{1}H-NMR spectroscopic studies of the products obtained.

TABLE 2. Characteristics of the Aromatic-Cycloaliphatic Polyesters[a]

Polymer code	Monomers	Yield, %	Softening interval, °C	η_{inh} dL/g
B-CP	Bisphenol A + CPC	82.1	183–190	0.31
Ph-CP	Phenolphthalein + CPC	49.8	248–253	0.17
HQ-CP	Hydroquinone + CPC	93.7	347–353	0.21
B-MCP	Bisphenol A + Me-CPC	78.0	165–170	0.25
Ph-MCP	Phenolphthalein + Me-CPC	47.7	215–220	0.18
HQ-MCP	Hydroquinone + Me-CPC	80.5	103–110	0.23
B-CB	Bisphenol A + CBC	51.9	98–100	0.19
HQ-CB	Hydroquinone + CBC	65.6	350–360	0.20

[a]CPC, Me-CPC, and CBC refer to acid chlorides of cyclopropane, 1-methylcyclopropane, and 1,2-cyclobutane dicarboxylic acids, respectively.

The prepared polyesters are soluble in a wide range of solvents at room temperature, but the best one seemed to be a phenol-1,2-dichloroethane (60/40, v/v) mixture, which was used for viscometric characterization of the products. Polyesters showed a satisfactory resistance toward acidic media, but were labile to alkali action. Products prepared from phenolphthalein, and especially those prepared with trans-1-methyl-1,2-cyclopropanedicarboxylic acid, were rapidly degraded on heating with 5% KOH solution. We have not found an explanation for the different behavior of cycloaliphatic polymers.

It is interesting to compare the melting properties of the polyesters obtained to those of aliphatic and completely aromatic polyesters. In this respect, some data were collected from the literature (Table 3), and it may be noted that our products generally have a medium position between the two types of polymers. Thus, as expected, the incorporation of cycloaliphatic units into polymer chains raises the softening temperature to 100°C over those of the aliphatic products, but still remain under those of the aromatic ones (compare Tables 2 and 3).

Thermal Stability of the Cycloaliphatic Polymers

To further understand the relationship of chemical structure to thermal stability, a thermogravimetric analysis of the synthesized products was undertaken. The results summarized in Table 4 and Fig. 7 show that the thermodegradative processes proceed in two or three steps. Also, the behavior of cycloaliphatic aromatic polyamides stands apart from other products having increased thermostability (400-450°C). High activation energies, especially for the symmetrical polymers, were calculated.

The random distribution of monomer units in statistical copolyamides is accompanied by destructive processes which start at 300-320°C, while the aromatic cycloaliphatic polyamides decompose over 400°C.

It is worth mentioning that weight losses at 400°C for the polyamides studied do not exceed 8-15%.

The best stability of the polyesters was found for poly-B-CP which decomposes over 350°C. It precedes the other polyesters in the following order: B-CP > B-CB > B-MCP.

The low thermal stability of the methylcyclopropane derivatives is probably due to the influence of the methyl group on the vicinal ester linkages which become more labile on thermal action:
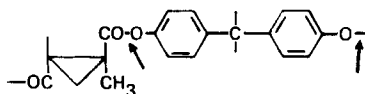
TABLE 3. Characteristics of the Aromatic- and Aliphatic-Aromatic Polyesters[a]

Polymer code	Monomers[a]	Softening interval, °C	η_{inh}, dL/g	Ref.
BT	Bisphenol A + CT	>360	1.3	13
BA	" + CA	63–85	0.31	14
PhT	Phenolphthalein + CT	>360	0.7	13
PhA	" + CA	120	0.45	15
HQT	Hydroquinone + CT	>500	–	16
HQA	" + CA	190–235	–	16

[a]CT and CA refer to terephthaloyl and adipyl chlorides, respectively.

TABLE 4. Thermal Behavior of Poly- and Copolyamides with Cycloaliphatic Units in the Chain

No.	Monomers[a]	Reaction order	E_a, kcal/mol			Decomposition domain, °C
			I	II	III	
1	CPC + p-FDA	1.0	-	67.06	-	480-620
2	CPC + Benzidine	2.4	-	120.47	-	430-630
3	CPC + 2,6-diaminotoluene	2.5	-	49.63	-	420-610
4	CPC + 3,3'-dimethoxy-benzidine	0.8	21.02	-	-	300-480
		1.7	-	29.1	-	550-750
5	CT(50) + CPC (50) + HMDA	2.5	49.5	-	-	300-380
		1.8	-	62.2	-	400-500
		1.5	-	-	97	500-580
6	CA (65) + CPC (35) + HMDA	2.5	64.4	-	-	320-520
		0.0	-	35.6	-	530-630
7	CS (50) + CPC (50) + HMDA	0.0	28.8	-	-	390-510
		2.5	-	89.5	-	515-605
8	CT + HMDA	2.0	54.5	-	-	305-395
		1.7	-	83.0	-	400-510
		1.6	-	-	67.3	515-630

[a]CPC, CT, CA, and CS are acid chlorides of cyclopropane, terephthalic, adipic, and sebacic dicarboxylic acids, respectively. Numbers in parentheses refer to the composition of the starting mixture.
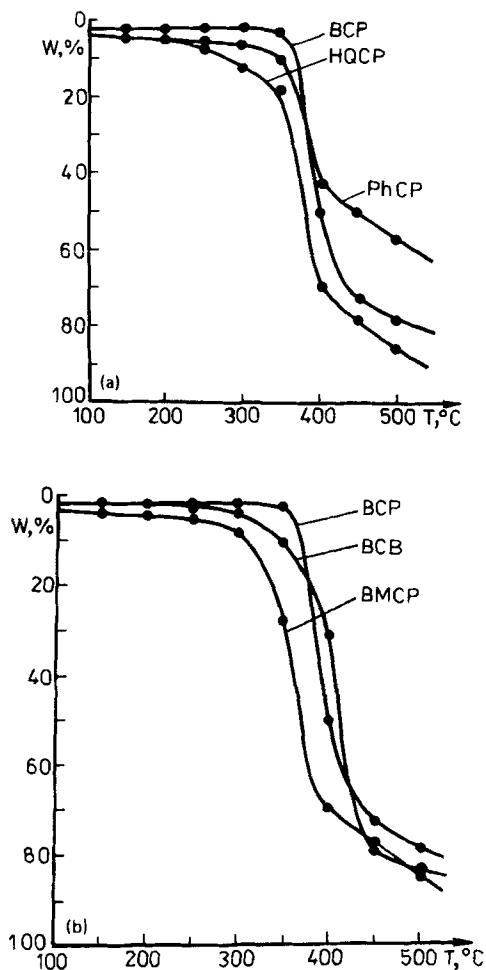
FIG. 7. Thermograms of aromatic cycloaliphatic polyesters. (a) Cyclopropane-based polyesters. (b) Bisphenol-A-based polyesters with various dicarboxylic acids.

Among the polymers derived from the same dicarboxylic acid (trans-CP), the highest stability was found for bisphenol A polyesters (Fig. 7b), all the other polymers being less stable: B-CP > Ph-CP > HQ-CP.

Although the HQ-CP product was expected to have the highest stability, it was probably not obtained due to the low molecular weight (η_{inh} = 0.21 dL/g). It might be that the increased content of aromatic units in phenolphthalein-based polymers increases the thermal stability.

In summary, the results obtained indicate that cycloaliphatic derivatives may be successfully used in the synthesis of polycondensation macromolecular compounds. These polymers may show new properties, good thermal and chemical stability, and interesting practical applications.

REFERENCES

[1] S. M. Aharoni, J. Appl. Polym. Sci., 25, 2891 (1980).
[2] D. Sek, Eur. Polym. J., 13, 967 (1977).
[3] C. Simionescu, E. Bouchi, and V. Bulacovschi, Mater. Plast., 15, 193 (1978).
[4] S. Caccamese, P. Maravigna, G. Montaudo, A. Recca, and E. Scamporrine, J. Polym. Sci., Polym. Chem. Ed., 17, 1463 (1979).
[5] S. Kohjiya and T. Tsuda, Makromol. Chem., 182, 215 (1981).
[6] F. C. Schryver, W. J. Feast, and G. Smets, J. Polym. Sci., Polym. Chem. Ed., 10, 1399 (1972).
[7] U.S. Patents 3,554,986, 3,622,440 (1971).
[8] R. J. Fraise and A. Freijaville, Bull. Soc. Chim. Fr., p. 219 (1970).
[9] E. Bouchi, V. Bulacovschi, A. Moga, E. Comaniţă, and C. Simionescu, Acta Polym., 30, 700 (1979).
[10] V. Bulacovschi, M. Dărângă, E. Boţan, and C. Simionescu, Ibid., 33, 527 (1982).
[11] N. Yamazaki, M. Matsumoto, and F. Higashi, J. Polym. Sci., Polym. Chem. Ed., 13, 1373 (1975).
[12] F. Higashi, S. Ogata, and Y. Aoki, Ibid., 20, 2081 (1982).
[13] P. Bajaj, D. N. Khanna, and G. N. Babu, Eur. Polym. J., 15, 1083 (1979).
[14] P. W. Morgan, J. Polym. Sci., Part A2, 437 (1964).
[15] A. A. Askadskij, Physical Chemistry of Polyarilates, Chimia, Moscow, 1968, p. 18 (in Russian).
[16] W. M. Eareckson, J. Polym. Sci., 40, 399 (1959).