

Synthesis and Characterization of Grafted Copolymers of Aromatic Polyimides and ϵ -Caprolactam

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ABSTRACT: Anionic polymerization of ϵ -caprolactam was performed in the presence of only 5 wt % of aromatic polyimides having five- and six-membered imide cycles and bearing hexafluoroisopropylidene, ether, fluorene, siloxane, phthalide, or SO_3H groups, both in the polymer backbone and as side moieties. The synthesized new copolymers were fully characterized by IR spectroscopy, thermomechanical analysis, dilatometry, and X-ray diffraction. Tough and frictional properties of the obtained copolymers were estimated as well. It was found that on the selection of polyimide activator it is possible to gain the

desirable control over the polymer properties, namely the gel-fraction content, phase composition, compression modulus, notched Izod impact strength, temperature of frictional contact, friction coefficient, etc. These investigations will facilitate the choice of the optimum macromolecular activator for the modification of both the synthetic method and the properties of the commercial polycaprolactam. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 577–586, 2009

Key words: ϵ -caprolactam; anionic polymerization; macromolecular activators; aromatic polyimides

INTRODUCTION

One of the important problems in lactam-based polyamide synthesis, namely the decrease in the reaction temperature, was solved more than 50 years ago by the use of special polymerization activators. Among the modern suggested activators for lactam anionic polymerization are macromolecular activators, which allow not only the decrease in the process temperature, but also the preparation of block and grafted copolymers.¹ Usually, the role of such macromolecular activators is carried out by the specially synthesized polymers having grafted acylactam groups. In contrast to that, for the first time we had demonstrated^{2–4} the principle possibility of the utilization of common (without any grafted acylactam side chains) aromatic polyimides (PI) as excellent activators for lactam anionic polymerization. Thus, a set of aromatic PIs, soluble in lactams melt, was successfully used in the polymerization of ϵ -caprolactam. It was proved^{2–4} that polymerization activation occurred at 150–180 °C due to the opening of the imide cycles in PI backbone under the action of lactam anionic polymerization catalyst, namely ϵ -caprolactam magnesium bromide. Along with this, it

is necessary to mention that on the utilization of Na- ϵ -caprolactam as another popular catalyst the anionic polymerization of ϵ -caprolactam (APC) with mentioned PIs did not proceed at elevated temperature.

The activating ability of PI was also studied by differential isothermal calorimetry method using various aromatic diimides as model compounds.³ It was found³ that the diimide activating ability is strongly dependent on the nature of the spacer between two five-membered imide cycles. These diimides containing hexafluoropropylidene or ketone groups proved themselves as best activating agents imparting the highest reaction rate. On the contrary, diimides based on aliphatic diamines do not activate the reaction.

Later on Youlee⁵ used the same technique and synthesized copolymers based on polycaprolactam (PCA) and PIs of the other type. However, copolymers prepared during this investigation and in Refs. 2–4 differ from those obtained in Ref. 5 by the presence of crosslinked structure, which greatly improves their operating characteristics as constructional materials.

To gain the desirable control over the obtained copolymer properties, we enlarged the set of PIs in the suggested study and carried out the detailed investigation of their influence on the APC. The most striking advantage of the suggested method concludes in

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TABLE I
Grafted Copolymers of PCA and Aromatic PIs I-V (5 wt %)

No	PI (η_{inh} , dL/g, in NMP)	Concentration of MgBr- ϵ -caprolactam, mol. %	Yield, %	η_{inh} , dL/g (in HCOOH)	Gel fraction in <i>m</i> -cresol, %	T_m^a , °C	T_{fl}^a , °C
1	I (1.25)	1	96	4.4	83	215	215
2	I (1.25)	0.75	99	4.8	69	220	233
3	I (1.25)	0.35	98	4.0	70	217	217
4	II (0.84)	1.2	97	–	71	202	242
5	II (0.84)	1	94	–	70	226	243
6	II (0.84)	0.5	96	4.3	31	219	232
7	II (1.40)	1	89	3.3	–	–	–
8	IIIa (0.28)	1	67	–	–	–	–
9	IIIb (0.24)	1	44	1.4	–	–	–
10	IV (1.02)	1	97	3.1	75	–	–
11	IV (0.62)	1.5	96	–	93	213	216
12	IV (0.62)	1	96	–	90	214	220
13	IV (0.62)	0.5	96	–	96	215	220
14	V (0.33)	1	0	–	–	–	–
15	– ^b	0.35	98	1.8	0	217	217

^a According to thermomechanical analysis.

^b *N*-Acetyl- ϵ -caprolactam (0.35 mol %) was used as an activator (for comparison).

the utilization of PIs, which activate the APC only by their own imide cycles, thus eliminating the necessity of any special functionalization before their use.

EXPERIMENTAL

Materials

Monomer, namely ϵ -caprolactam, was recrystallized from benzene and dried thoroughly in high vacuum at 50°C before use.⁴

Catalyst, ϵ -caprolactam magnesium bromide, was prepared by interaction of synthesized ethyl magnesium bromide with ϵ -caprolactam according to the published procedure.⁶ The obtained catalyst was characterized by IR spectroscopy, which was in a full agreement with Ref. 6.

PIs synthesis

Aromatic PIs I and II were synthesized by one-step polycondensation in *m*-cresol,⁷ PI III by polycondensation in supercritical CO₂,⁸ and PIs IV and V by polycondensation in ionic liquids.⁹

Copolymers preparation technique

All the manipulations were carried out under inert atmosphere. APC in the presence of aromatic PIs was performed in the glass tubes equipped with an argon inlet and outlet. After the dissolution of aromatic PI in ϵ -caprolactam at 150°C, the separately prepared solution of ϵ -caprolactam magnesium bromide in ϵ -caprolactam was quickly added. The reaction mass was stirred at 150°C for 1 min, then the temperature was raised to 180°C and finally the

reaction mixture was kept at 180°C for 1.5 h.⁴ The obtained polymer solids were slowly cooled down to room temperature at a rate of 2.5°C/min. All the prepared copolymers after the synthesis were milled into small pieces and extracted with methanol under stirring for 24 h, and then were dried in vacuum at 70°C.

For gel dissolution, the weighed copolymer samples were placed in the formic acid for 1 week at room temperature, whereupon some crosslinkages were destroyed and the formation of viscous solution was observed (copolymer : HCOOH weight ratio is 1 : 9).

The reaction parameters as well as the conversion and the inherent viscosity of the obtained copolymers are summarized in Table I.

Measurements

For the estimation of copolymer's gel fraction (GF), the milled samples were extracted with *m*-cresol for 48 hrs and then thoroughly washed with methanol in Soxhlet apparatus. The GF was defined as:

$$GF(\%) = \frac{(W_o - W_e)}{W_o} \times 100,$$

where W_o and W_e are the weights of polymer samples before and after the extraction.

Films were cast from 10% polymer solution in formic acid on the glass plates with further slow solvent evaporation at 70°C, and then they were dried in vacuum at 70°C. The polymer film thickness was varied in the range of 25–50 μ m. Polymer films tough properties (σ - tensile strength [kPa] and

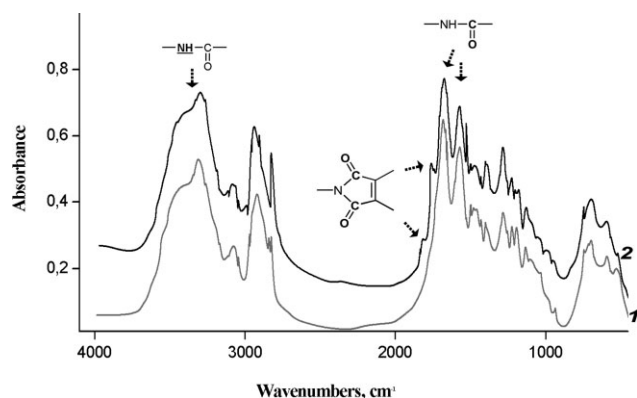


Figure 1 FTIR spectra of plain polycapramide (1) and its copolymer with PI II (2).

ϵ - elongation [%]) were estimated at room temperature using dynamometer "Polyani" (Hungary).

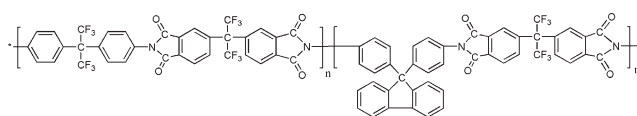
IR spectra were recorded using Nicolet Magna - 750 Fourier IR spectrometer. Inherent viscosities (η_{inh}) were measured using Ostwald capillary viscometer (0.05 g of polymer in 10.0 mL of HCOOH at 25.0°C). Thermomechanical study was done at a dead load equal to 8×10^{-2} MPa and at a heating rate of 3°C/min on samples with 2-mm thickness. In contrast, the dilatometric analysis was performed with changing load on a UIP-70M analyzer (Russia) using heating rate of 2.5°C/min. The used load was varied in the range of $0.1-2 \times 10^{-3}$ MPa. The samples prepared by cutting the standard dimensions were placed into a steel caps with 6-mm diameter. For dilatometric investigations, the samples represented bars with 4 mm wide, whereas for thermomechanical tests, cylinders with a diameter of 4 mm and a length of 0.8 mm. Hollow quartz rod with external diameter of 4 mm and a spherical tip was used for dilatometric measurement, whereas in thermomechanical studies, the hollow quartz rod had a diameter of 1.8 mm and the invar indenter on the cylindrical tip. The notched Izod impact strength and flexural modulus for polymer blocks were determined on a PDM-10 and "Dinstat" devices, respectively. Thermofrictional examinations were measured using I-47 butt friction machine.¹⁰

The diffraction patterns of standard PCA and its copolymers have been examined on automated powder diffractometer DRON-3 ("Burevestnik," Russia) using the reflective Bragg-Brentano geometry. The data acquisition parameters were set as follows: CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$), secondary-beam pyrolytic graphite monochromator, generator operation at $36 \text{ kV} \times 20 \text{ mA}$, continuous $\theta/2\theta$ scanning with an angle step of 0.1° and a scanning rate of $1^\circ/\text{min}$. Rectangular bars for the diffraction measurements were cut directly from polymer solids obtained during the polymerization and had an approximate size of $10 \times 5 \times 3 \text{ mm}^3$.

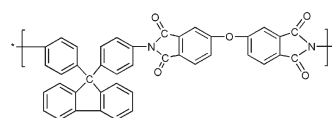
RESULTS AND DISCUSSION

Synthesis and the choice of PI structures

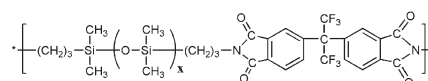
For the achievement of the cited target, several tailored aromatic PIs (Fig. 1, I - V) with five- and six-membered imide cycles were synthesized and studied in APC process



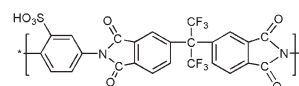
I ($n : m = 1 : 3$)



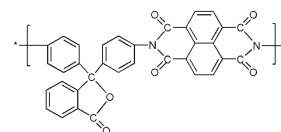
II



IIIa ($x=10$), **IIIb** ($x=2$)



IV



V

Discussing the suggested polymer structures, it is necessary to mention that CF_3- and cardo groups were specially introduced in all PIs for the improvement of final PI's solubility in the ϵ -caprolactam melt. PI IV was chosen due to the presence of $\text{SO}_3\text{H}-$ groups that were expected to promote the formation of grafted copolymers with specific properties.

The choice of reaction media for PIs synthesis was determined by several factors including the structure of monomers and the requirements for polymer molecular weight. Following our previous investigations,^{8,9,11} high molecular weight PIs IIIa, IIIb, and IV, containing siloxane or pendant sulphuric acid groups, can not be obtained by well-known one-step polycondensation in *m*-cresol, which is suitable for the preparation of other polyimides. Therefore, PI III was successfully obtained in a satisfactory yield and high molecular weight by using of supercritical CO_2 technique.¹¹ At the same time, PIs IV and V were successfully synthesized in ionic liquids due to the

following reasons: first, IIs can dissolve aromatic diamines containing side sulphuric acid groups without the addition of triethylamine and second, they activate the formation of PIs in the absence of any added catalyst and lead to the preparation of high molecular weight polymers.^{8,12-16} The viscosity characteristics of all obtained PIs are presented in Table I.

It was found that PIs **I**, **II**, **IIIb**, and **IV** are soluble in ϵ -caprolactam melt at 150°C with the exception of **IIIa**, which was dissolved only at 180°C. At that the maximum PI concentration, that can be achieved was equal to 5 wt %.

Anionic polymerization of ϵ -caprolactam

APC was carried out in the optimal conditions elaborated earlier,²⁻⁴ namely, with 1 mol % of ϵ -caprolactam magnesium bromide as a catalyst in the presence of only 5 wt % of the above-mentioned PIs and at a temperature rise from 150 to 180°C (3°C/min). The exception was made for APC in the presence of PI **IIIa**. In this case, the polymerization was performed at a constant temperature equal to 180°C. The grafting density was controlled by the change of catalyst concentration at a constant composition of macromolecular activator (Table I, entries 1-3, 4-6, etc.). It was proposed that some of the polymer properties can be changed by tuning of the grafting density during the polymerization process. However, comparing the results of APC with different amounts of chosen catalyst (Table I), it was concluded that grafting density plays rather insignificant role over polymer melting and flow points. In such a way, the maximum difference in copolymer melting point was found to be 24°C (Table I, entries 4 and 5), whereas in flow point the difference reached 18°C (Table I, entries 1 and 2). Polymerization of ϵ -caprolactam with PIs **I**, **II**, and **IV** proceeded with the quantitative yield, i.e., with the highest possible yield for the cited experiment temperature, whereas in the presence of PIs **IIIa** and **IIIb** conversion decreased to 67 and 44%, respectively. The presence of fluorine groups along with ether groups in PI **II** makes it more effective activator in comparison with previously studied one,² containing both cited groups and the isopropylidene fragments (97 and 29% of monomer conversion, respectively). The decrease in ϵ -caprolactam conversion during its polymerization with PIs **IIIa** and **IIIb** in comparison with the same process in the presence of PIs **I** and **II** can be explained by the electron donor effect of aliphatic fragment at the N atom of imide cycle, which in its turn causes decrease in electrophilicity of imide carbonyl C atoms (see below the scheme of polymerization mechanism). Such explanation is in a full agreement with our

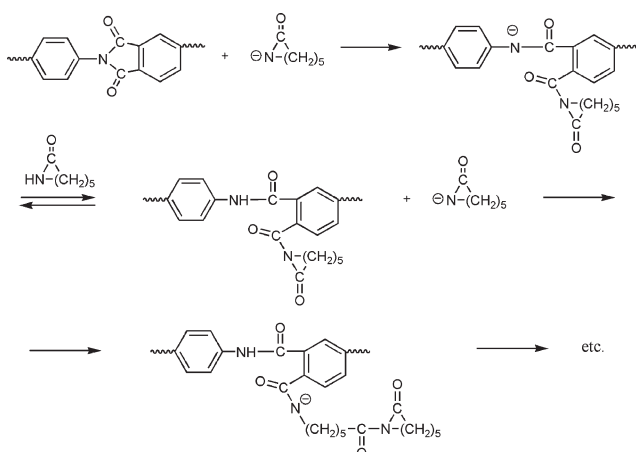
results on APC process performed with model compounds, namely, with diimides.²⁻⁴

No polymer formation was observed when five-membered imide cycles were changed to six-membered ones (PI **V**). This can be clarified by known¹⁷ higher stability of 1,4,5,8-naphthoylene imide cycles to nucleophiles action, which prevents the reaction between the PI's backbone and ϵ -caprolactam magnesium bromide catalyst and as a result the activation of APC does not occur.

All the obtained copolymers represent colored substances (from yellow to dark brown) and only swell in some solvents, such as *m*-cresol, formic, and sulfuric acids. The latter fact confirms their partial network structure since both linear and branched PCAs are soluble in the above solvents. It is well known that three-dimensional structure is typical for PCA obtained in the presence of polyfunctional activators. However, in our case, linkages have imide nature and are formed due to the interaction of amide anions and the terminal PCAs acyl lactam groups.¹⁸ Therefore, the GF in *m*-cresol for all the obtained copolymers is rather high (>69%) and sometimes reaches 96% (Table I, entry 13). Such result can be explained by the formation of additional crosslinked bonds due to the interaction of PI SO₃⁻ anions with PCA acyllactam groups at sufficiently high density of polyamide chains grafting.

In all suggested APC reactions, aromatic PIs were completely incorporated into the resultant copolymer structure. This was confirmed by the investigation of copolymers conversion after the extraction with methanol and chloroform. The choice of the mentioned solvents was due to the fact that all relevant PIs are soluble in chloroform and completely insoluble in methanol, whereas ϵ -caprolactam can be easily dissolved in both solvents. Thus, at first the resultant copolymers were thoroughly washed with methanol to get rid of unreacted ϵ -caprolactam. Then, they were extracted with chloroform whereupon their weight was compared with that after washing with methanol. The invariability of polymer weight after the chloroform extraction can serve as a good evidence of the complete absence of free PI in the obtained grafted copolymers. Moreover, the IR spectra of the copolymers after extraction (Fig. 1) contain bands characteristic for both amide and imide structures. Thus, the signals at 3300 cm⁻¹ relate to the NH valent vibration of amide bond and at 1640 and 1538 cm⁻¹ to amide-I and -II bands, respectively. Besides the mentioned bands copolymer spectra (Fig. 1, line 2) contain the signals related to PI, namely at 1770 and 1720 cm⁻¹ (imide C=O groups) as well as at 1510 cm⁻¹ (aromatics).

A typical reaction path for the formulation of PCA graft copolymers with aromatic PIs is presented below:



The validity of such scheme is confirmed by the following factors: first, the polymerization of ϵ -caprolactam in the absence of PI at cited temperature does not practically proceed; second, it is well known that substances having imides groups promote anionic polymerization of lactams; third, the proved fact of the full insertion of aromatic PIs in the copolymer macromolecules (see *vide supra*); and finally, the presence of crosslinked structure in the obtained copolymers. It is necessary to underline that relatively low-PI concentration (5 wt %) in copolymers composition as well as the insolubility of the latter in common organic solvents make impossible any direct investigation (by NMR method, for example) of copolymers structure and determination of the ratio of noncycled imides in particular.

Characterization of copolymers

The crystalline structure of customary PCA and PCA-based copolymers obtained in this work was studied by X-ray diffraction method. All investigated samples revealed similar diffraction patterns, although they were not fully identical. Figure 2 demonstrates the diffraction patterns of plain PCA and its copolymer with PI I synthesized with 1 mol % of catalyst as well as their profile deconvolution (several Gaussians superimposed on a linear incoherent scattering background). The patterns revealed two distinct relatively narrow peaks at $\sim 20^\circ$ (with full widths at half maxima in a range of $0.7\text{--}0.9^\circ$) and at 24° (with full widths at half maxima near $1.0\text{--}1.5^\circ$). Nevertheless, an adequate pattern fit required the introduction of two additional substantially broader components at $20\text{--}21^\circ$ (with full widths at half maxima near $11\text{--}14^\circ$) and at 22° (with full widths at half maxima near $5.3\text{--}5.6^\circ$). The found difference between the diffraction patterns of all studied samples is the intensity redistribution of these four characteristic components. It is known^{19–21} that PCA can be rou-

tinely obtained as one of the two possible crystalline polymorphs, *viz.*, monoclinic α or pseudo-hexagonal γ or generate the amorphous form as well. All these forms coexist usually together in one sample. The total degree of crystallinity, relative amounts of the two polymorphs, and their overall degrees of structural order are strongly dependent on the preparation and crystallization conditions of each specific sample.

The two characteristic narrow peaks at ca. 20 and 24° (see Fig. 2) are clearly attributable to the α modification of PCA. The first peak is identified at 200 cm^{-1} and corresponds to the direction of strong intermolecular hydrogen bonds between the neighboring PCA macromolecules (the crystallographic axis a),²² whereas the second peak is related to the unresolved $002/202$ doublet. A broader feature at around 22° can be assigned to the γ phase with an overall low degree of structural order. The amorphous component is manifested as a very broad halo centered at 20° . The fractions of the α , γ , and the amorphous phases along with relative intensities of the two major lines of the α phase calculated from the experimental patterns according to the standard procedures are compiled in Table II. The $(I_{200} + I_{202})/I_{002}$ value varies over the wide range from 1.4 to 7 (Table II) for the PCA-based investigated copolymers which is probably due to the change of average orientation of polymer macromolecules on the reaction parameters variation. It is noticeable that the mentioned $(I_{200} + I_{202})/I_{002}$ ratio, *i.e.* smaller

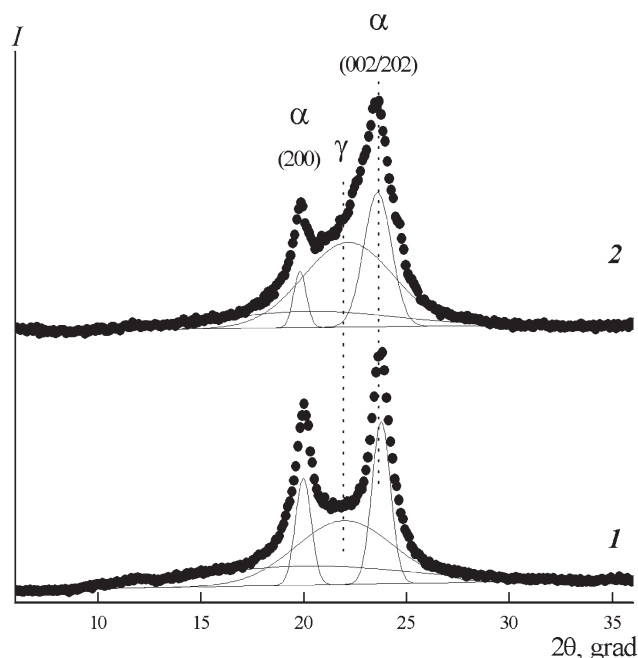


Figure 2 Experimental diffraction patterns (dots) of PCA (1) and its copolymer with 5 wt % of PI I (2) and the results of their profile deconvolution (lines).

TABLE II
Phase Composition of Copolymers According to the Data of Diffraction Patterns Profile Deconvolution

No	PI (η_{inh} , dL/g)	Concentration of MgBr- ϵ -caprolactam, mol %	Fraction of α form, %	Fraction of γ form, %	Fraction of amorphous form, %	$(I_{200} + I_{202})/I_{002}$
1	–	0.35	34	40	26	1.8
2	I (1.25)	1.00	32	50	18	4.8
3	II (1.40)	1.00	29	41	30	5.9
4	IV (1.02)	1.00	30	45	25	7.0
5	IV (0.62)	1.00	22	44	34	2.3

for unmodified PCA and its copolymer with PI IV having 0.62 dL/g viscosity, than for all other PCA copolymers with PIs I, II, and IV characterizing by higher η_{inh} (Table II, entries 1, 5, and 2-4). The content of highly ordered α phase in the copolymers is obviously independent on the PIs nature; however, it is influenced by the molecular weight of used PI (Table II, entries 4 and 5). Apparently, PIs main backbone at sufficient density of grafting is acting as additional orienting function for grafted PCA chains. Thus, the copolymer with the largest grafting density is characterized by the biggest fraction of less-ordered γ phase (Table II, entry 2). Finally, polymerization of lactam as well as the crystallization of its copolymer with PI as an activator of indirect action, proceeds more slowly than with traditional monofunctional activators,² which in its turn also influences the crystalline structure of obtained copolymers.

Heat resistance of the synthesized copolymers was studied by thermomechanical method. The appear-

ance of thermomechanical curves of the copolymers containing low molecular weight PI I or IV (η_{inh} 0.62 dL/g) were found to be identical to thermomechanical curve of the standard PCA (Fig. 3, curve 1).²³ The slope angle of the thermomechanical curves depends on the concentrations of both the polymerization catalyst and the dissolved PI and is distinctly changing in the region above the melting point. Interestingly, the flow temperature of all PCA copolymers with PI II at any catalyst concentration exceeded the melting temperature of standard PCA (Table I and Fig. 3, curves 2-5). The thermomechanical curves of such copolymers contain clearly observed high elasticity region above the melting point of PCA (Fig. 3). This region slightly increases with the increase in MgBr- ϵ -caprolactam concentration, which influences the functionality of PI activator. Thus, because of the decrease in PCA-grafted chains length, the melting point of the copolymer is reduced at a catalyst concentration of 1.2 mol %. The similar high-elasticity region is also observed for the copolymers containing 3 or 5 wt % of PI II. It can be concluded that PCA copolymers with PI II are able to keep the integrity of their shape at a temperature higher than plain PCAs melting point due to the transfer to the high-elasticity state. This fact is in a good agreement with thermomechanical data for PCA synthesized in the presence of polyfunctional activators such as *N*-acryloyl- ϵ -caprolactam copolymers.²⁴

The T_g of PCA and its copolymers with PIs II and IV (η_{inh} 1.02 dL/g) as well as their linear thermal expansion coefficients in the regions below (L_1) and above (L_2) glass transition temperature were determined by dilatometry measurements (Fig. 4). In all cases, T_g of the studied copolymers exceeds the corresponding parameter for standard PCA. Values $L_1 \times 10^5$ and $L_2 \times 10^4$ for PCA and its the copolymers with PIs mentioned above were found to be 7.58 and 1.45, 8.22 and 1.88, 8.09 and 1.44, respectively.

Figure 5 demonstrates another thermomechanical curves for PCA and its copolymers with PIs. The difference is consisted in fact that thermomechanical tests were carried out in the temperature range from -100 to ~ 300 °C at a variable load. It is noticeable,

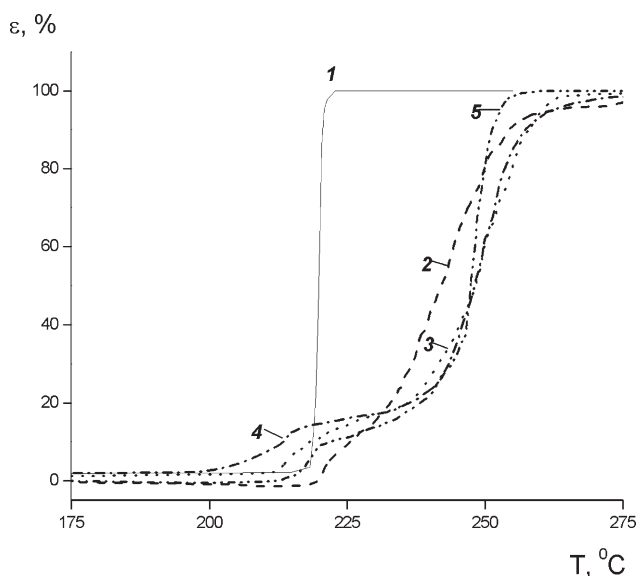


Figure 3 Thermomechanical curves of PCA (1) and its copolymers with 5 wt % of PI II at MgBr- ϵ -caprolactam concentration: 0.5 mol % (2); 1 mol % (3); 1.2 mol % (4) as well as with 3 wt % of PI II at MgBr- ϵ -caprolactam concentration equal to 1 mol % (5).

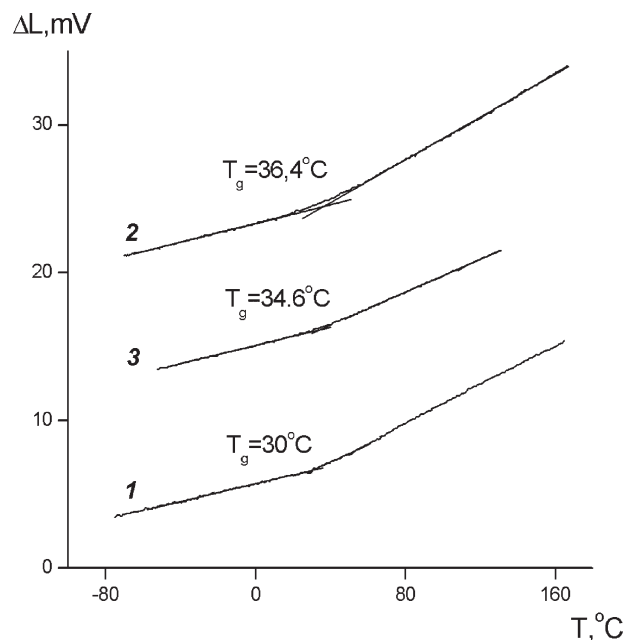


Figure 4 Linear dilatometry curves of plain PCA (1) and its copolymers with PI II (η_{inh} 0.86) (2) and IV (η_{inh} 1.02) (3) at a heating rate of 2.5°C/min.

that the reversible deformation for all copolymers was found to be 2.6 – 9.6% at temperatures lower than their T_g , whereupon it increases at temperatures higher than T_g with the exception for copolymer based on PI II. Moreover, this reversible deformation is higher for all studied copolymers than for standard PCA and strongly depends on PI nature. Summarizing data from Figure 5 and Table III (see below), it can be concluded that the above-mentioned deformation directly correlates with the

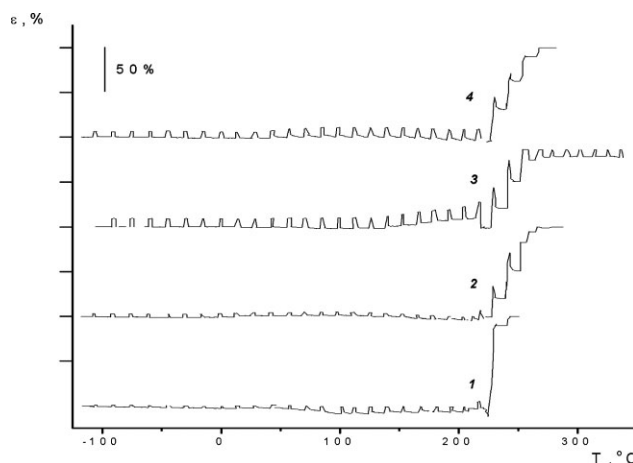


Figure 5 Thermomechanical curves of PCA (1) and its copolymers with PIs I (2), II (3), and IV (4) obtained through loading (0.1 MPa)/consistent unloading (2×10^{-3} MPa) procedure at a heating rate of 2.5°C/min.

values of impact strength for PCA and its copolymers.

It was found that copolymers based on PCA and PIs I, III, and IV (η_{inh} 1.02 dL/g) became soluble in formic acid after 1-week treatment with this acid at room temperature. It is supposed that this is due to the disruption of easily hydrolysable bridged aliphatic imides linkages.^{2,18} Surprisingly, significantly more prolonged acid treatment, ca. 1 month, is required to reach the dissolution of copolymers based on PI II. Such behavior can be explained by the presence of flexible ether groups in the PI II backbones and as a consequence by the interaction of the aromatic amide type A anions with acylactam groups of growing PCA macromolecules. The imide groups of such crosslinkages are involved in the

TABLE III
Mechanical Properties of the Copolymers Composed from PCA and 5 wt % of Pi

PI (η_{inh} , dL/g)	Concentration of MgBr- ϵ -caprolactam, mol %	Film			Block		Notched Izod impact strength A_{Iz} , kJ/m ²
		Tensile			Compression		
		σ , MPa	ϵ , %	$E \times 10^{-3}$, MPa	σ , MPa	$E \times 10^{-3}$, MPa	
I (1.25)	1	63	32	2.4	60	1.5	14.7
I (1.25)	0.75	65	133	2.0	47	1.1	18.2
I (1.25)	0.35	61	69	2.2	30	0.7	14.5
II (0.84)	1.2	–	–	–	–	–	10
II (0.84)	1.0	64	38	2.4	45	1.3	>50
II (0.84)	0.5	75	81	2.7	50	1.4	>50
II (1.40)	1.0	–	–	–	30	0.6	–
IIIa (0.28)	1.0	48	20	1.6	–	–	–
IV (0.62)	1.5	–	–	–	54	1.1	20
IV (0.62)	1.0	–	–	–	54	1.1	8.7
IV (0.62)	0.5	–	–	–	53	1.0	7.7
IV (1.02)	1	51	21	1.8	33	0.7	28.5
– ^a	0.35	71	80	1.9	53	1.7	4.3 ²⁵

^a N-acetyl- ϵ -caprolactam (0.35 mol %) was used as an activator.

TABLE IV
Frictional Properties of the Copolymers Composed of PCA and Various PIs

No	PI (η_{inh} , dL/g)	Temperature difference in frictional contact, °C ^a		Deterioration of the polymeric sample, %	Friction coefficient	
		1 hr	2 hr		1 hr	2 hr
1	–	0 ^b	0 ^c	100 ^d	0.69	0.94
2	I (1.25)	19	27	62.5	0.50	0.40
3	II (1.6)	22	28	12.5	0.63	0.50
4	IV (0.62)	14	5	12.5	0.40	0.65
5	VI (0.46)	9	19	50	0.50	0.48
6	VI (1.45)	6	8	75	0.50	0.56

^a Relative to plain PCA.

^b The temperature of frictional contact is 57°C.

^c The temperature of frictional contact is 70°C.

^d Deterioration of the polymeric sample is 8×10^{-4} g.

conjugated aromatic PI chain and as a result their chemical stability is increased in comparison with the imide groups formed during the interaction of aliphatic amide anions (type B), that are spaced away from the PI chain. Gels based on copolymers derived from PCA and PI IV (η_{inh} 0.62 dL/g) remained insoluble even upon their treatment in the acids for more than 2 months. The above-mentioned fact can be explained by the presence of additional crosslinks, formed by the SO₃H– groups.

The properties of copolymers films were found to be practically the same as the properties of plain PCA films (Table III). In such a way, their tensile strength is slightly smaller than that of PCA films with the exception of the film based on copolymer with PI II. The rigidity of the films obtained from copolymers with PIs I and II exceeds the corresponding parameter for PCA film in 5–37% and depends on the catalyst concentration. The sample prepared from PCA and PI II catalyzed by 0.75 mol % of MgBr- ϵ -caprolactam is characterized by the highest elongation equal to 133%.

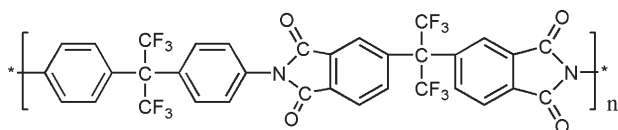
Along with films, the mechanical properties of the molds derived from copolymers were studied in detail and are summarized in Table III. The polymer compression modulus is varied in the range of 600–1700 MPa. The notched Izod impact strength (A_k) was found to be strongly dependent on PI structure and changed from 8.3 to 50 kJ/m². Copolymers based on PCA and PI II were characterized by the highest value of impact strength (>50 kJ/m²) and did not destroy during the whole time of testing. This result significantly exceeds the corresponding characteristics of the samples synthesized in the presence of known mono- and multifunctional activators, such as *N*-acetyl- ϵ -caprolactam, *N*-metacryloyl- ϵ -caprolactam, *N*-acryloyl- ϵ -caprolactam (4.3–6.9 kJ/m².²⁵) or even with the activator of three-dimen-

sional structure, namely, copolymer of *N*-acryloyl- ϵ -caprolactam (34 kJ/m²).²⁴

The flexural modulus of all novel copolymers was higher than 150 MPa. The investigated samples demonstrated the behavior similar to elastic materials. In such a way, copolymers with PI II and IV (η_{inh} 0.62 dL/g) bend without the demolition up to 86° corner, maintaining a pressure of 165 and 195 MPa, respectively (for comparison, unmodified PCA is bending to the corner not higher than 40° and standing the maximum stress of 140 MPa). These exceptional copolymer's tough properties can be explained by the reinforcing effect of aromatic PIs and by the high content of GF.

The influence of PCA chain grafting density on the copolymers properties was examined as well (Table III). Copolymers based on PI I (η_{inh} 1.25 dL/g) with the reduction of ϵ -caprolactam magnesium bromide concentration from 1 to 0.35 mol % demonstrated double decrease in flexibility modulus, 28% change in impact strength, 15% decrease in crystallinity and invariability of flexural strength, which for all samples was higher than 150 MPa. In contrast to the properties of copolymers with PI II did not practically change even at double reduction of the catalyst concentration. Finally, on investigation of copolymers based on PI IV (η_{inh} 0.62 dL/g), the impact strength was significantly increased (2.5 times) with the increase in catalyst concentration. At a constant catalyst concentration, the impact strength of copolymers based on PIs I and IV was improved in 1.8 and 3.3 times on rising their inherent viscosity from 0.32 to 1.25 dL/g and from 0.62 to 1.02 dL/g, respectively. This is directly related to the increase in PI activator's functionality. At the same time, when inherent viscosity of PI II was increased from 0.84 to 1.4 dL/g, the compression modulus of the copolymers was reduced 2.2 times.

It is well known that PCA is widely used in friction units.²⁶ Therefore, the investigation of new copolymers and their tribological properties was of particular interest. Table IV demonstrates the influence of PI chemical structure and its molecular weight on the tribological properties of the relevant PCA copolymers. Apart from the already-mentioned PCA copolymers with PIs I–V the tribological properties of the copolymer with PI VI were also investigated (Table IV, entries 5 and 6).



VI

At that, the influence of PI VI on the APC process was studied previously.^{2–4} It was established that all the studied copolymers showed stable friction without any mass transfer from polymer sample to the steel rider. In contrast to that, the friction of unmodified PCA was accompanied by a scratch intensifying in time, as well as by the transportation of polymer traces on a contact body. As it is seen from Table IV, copolymers with F-containing PIs (I, IV, and VI) are characterized by the reduced temperature of frictional contact, decreased abrasion of the polymeric sample and downturn of friction factor in comparison with standard PCA. These results can be explained by the fact that in accordance with^{10,27} such PIs enrich the surface of copolymer samples during the friction process. Furthermore, the decrease in the friction coefficient in comparison with plain PCA is caused by the presence of cross-linked structure and by higher crystallinity. Among the studied samples, the copolymer based on PI IV had the lowest abrasion apparently due to the highest content of GF. Interestingly, that copolymer containing fluorine-free PI II was also characterized by downturn of frictional contact temperature and friction coefficient in comparison with unmodified PCA (Table IV).

CONCLUSIONS

Summarizing the obtained results, it can be concluded that PI chemical structure and especially its molecular weight greatly influence the yield and the properties of nascent copolymers. Therefore, it was found that on the careful selection of PI activator, it is possible to modify PCA and to gain the desirable control over the GF content, phase composition, compression modulus, notched Izod impact strength,

temperature of frictional contact, friction coefficient, and the other polymer characteristics.

The suggested method allows the preparation of the cured copolymers that differ from the commercial Nylon 6 by improved properties, namely, the notched Izod impact strength and flexural strength are significantly increased and exceed 50 kJ/m² and 150 MPa, respectively. The flexibility is greatly improved (the samples can bend without the demolition up to $\sim 90^\circ$ corner maintaining a pressure of 195 MPa) and the reversible deformation under variable load is dramatically increased in the temperature region of 100–300°C.

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