

Polyamides and Polyester Amides Based on Triarylmethane-Type Diamines

T. A. Borukayev^a, A. V. Orlov^b, R. Z. Oshroyeva^a, Kh. V. Mashukov^a, and A. K. Mikitayev^a

^aKabardino-Balkarian State University, Nalchik, Russia

^bTopchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russia

e-mail: boruk-chemical@mail.ru

Abstract—Novel aromatic polyamides and polyesters containing triarylmethane fragments in the main chain were obtained. It was shown that the obtained polymers were easy to process from solution and from melt. It was found that the synthesized polymers demonstrated enhanced thermal stability, and the films based on polyamides exhibited high strength indicators. It was found that polyamidoesters demonstrated properties of liquid crystals.

Keywords: polyamides, polyamidoesters, synthesis, properties

DOI: 10.1134/S2075113316010032

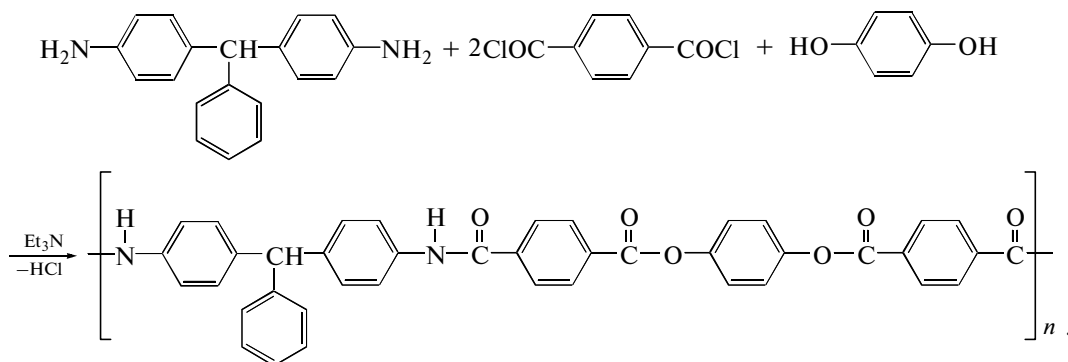
Aromatic polyamides (PA) and polyamidoesters (PAE) exhibit unique properties such as thermal shock resistance, impact resistance, and thermal and chemical stability [1–3]. Nevertheless, high melting and softening temperatures, limited solubility, and significant rigidity of macromolecules hinder processing of these polymers into products. In this connection, aromatic PA and PAE, which would retain a characteristic high level of physical and mechanical properties and at the same time would be easy to process from solution or melt, have attracted significant interest of researchers.

The use of derivatives of 4,4'-diaminotriphenylmethane as initial diamines provides considerable promise for solving this problem. Owing to the chemical structure, their bulky substituents could affect favorably the manufacturability of polymers. More-

over, the given 4,4'-diaminotriarylmethanes can be easily produced via a one-step process with high yield from commonly available compounds.

This study deals with the synthesis of aromatic PA and PAE based on triarylmethane-type diamines and investigation of their general properties: thermal and mechanical characteristics.

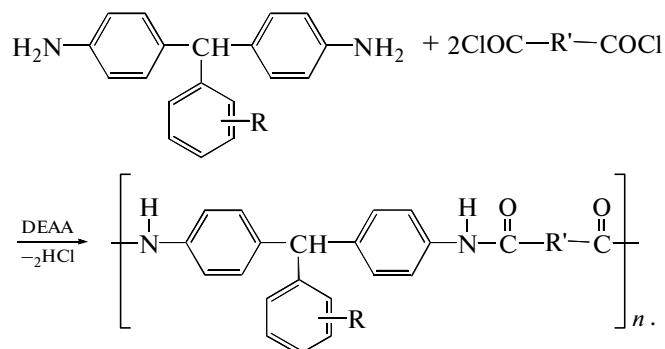
The PA and PAE based on triarylmethane-type diamines were produced in this work via low-temperature polycondensation and co-polycondensation of initial monomers in an N-methylpyrrolidone solution (MP) in an inert atmosphere. 4,4'-Diaminotriarylmethane, hydroquinone, and dichloroanhydrides of tere- and isophthalic acid were used as monomers. The reaction scheme for production of PAE can be represented as follows:



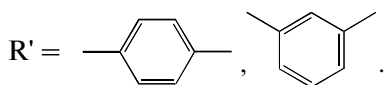
MP solvent and triethylamine played the role of HCl acceptors.

Preparation of PA via low-temperature polycondensation of diamines with dichloroanhy-

drides of tere- and isophthalic acids in a diethylacetamide (DEAA) solution in an inert gas atmosphere can be represented by the following scheme:



where R = H, CH₃;



Other compounds were also used as solvents and HCl acceptors: N,N-dimethylacetamide (DMAA) and N-acetylpiperidine (AP). It was found that the use of DMAA and AP in the case of PAE resulted in the reduced viscosity of the products of polycondensation. The PA obtained in the presence MP and AP as solvents demonstrate low viscosity. On the other hand, if co-polycondensation or polycondensation was conducted in DMFA, the formed products demonstrated very low viscosity. The production of high molecular weight polymers was hindered by the side reaction of diamine with the solvent that proceeded to a large depth.

When the effect of monomer concentration on the viscosity of polymer was investigated, it was estab-

lished that the polymers with maximum viscosity parameters were produced if the total concentration of monomers was 0.6 mol/L for PAE and 1 mol/L for PA. The duration of the process of polymer production was 120 min for PAE and 90 min for PA. The yield and some properties of PA and PAE are presented in Table 1.

The synthesized PAE were partially crystalline (XRD data) white compounds. The PAE and PA were readily dissolved in amide solvents (DMAA, DMFA + 5% LiCl, MP, DMSO, and AP), forming highly concentrated solutions. The transparent films were cast from the PA + DMFA solutions by pouring onto a glass support followed by thermal drying. As a result, the PA based on 4,4'-diaminotriphenylmethane and dichloroanhydrides of tere- and isophthalic acid had tensile strength of 8.9 and 6.0 kgf/mm² and relative elongation at breakage of 9 and 8%, respectively (Instron-1122 testing instrument, speed of breakage of 5 mm/min).

The structure of obtained polymers was confirmed with the help of IR spectroscopy (Spekord M-82IR spectrometer, range of 400–4000 cm⁻¹) and elemental analysis. The elemental composition of the products of polycondensation was close to the calculated values.

Analysis of the spectra of the polymers based on 4,4'-diaminotriphenylmethane and dichloroanhydride of terephthalic acid makes it possible to establish the presence of the following groups: monosubstituted benzene ring (bands at 700 and 1110 cm⁻¹), 1,4-disubstituted benzene rings (bands at 785, 1015, 1225, and 1320 cm⁻¹), the bands at 1510 and 1560 cm⁻¹ correspond to C–C valence vibrations, the 1700 cm⁻¹ band corresponds to a carbonyl group, the band with bend at 3420 cm⁻¹ corresponds to an amino group, and several bands in the range 3000–3100 cm⁻¹ correspond to vibrations of the C–H valence bond of aromatic rings (Fig. 1).

Introduction of side substituents into triphenylmethane, as well as the use of dichloroanhydride of

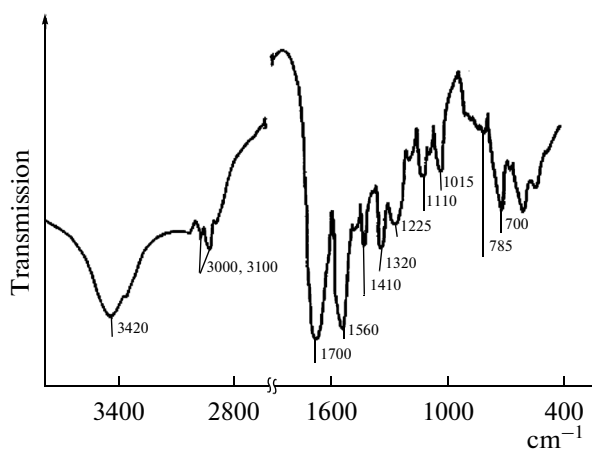


Fig. 1. IR spectrum of PA based on 4,4'-diaminotriphenylmethane and dichloroanhydride of terephthalic acid.

Table I. Yield and properties of PA and PAE based on triarylmethane-type diamines

No.	Polymers	Monomer concentration, mol/L	Yield, %	Solvent	η_i , dL/g
I		1.0	98.3	DEAA	1.5
II		1.0	97.1	DEAA	1.2
III		1.0	98.4	DEAA	1.5
IV		1.0	98.1	DEAA	1.3
V		0.6	90.8	MP	0.6
VI		0.6	91.1	MP	0.6

Intrinsic viscosity (η_i , dL/g) was determined in DMFA solution (0.5 g per 100 mL of DMFA) using an Ubbelohde-type viscometer at 20°C.

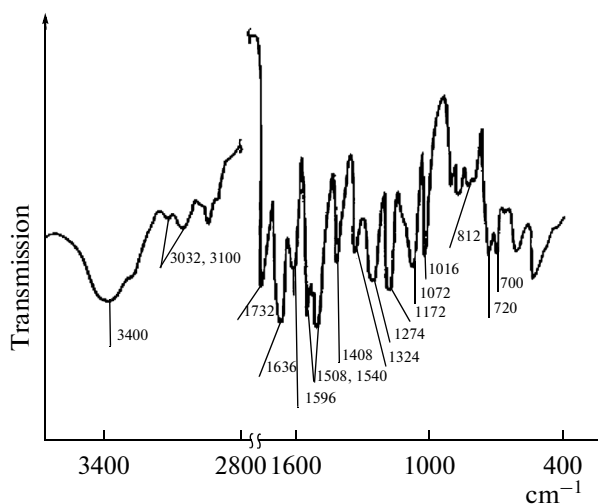


Fig. 2. IR spectrum of PAE based on 4,4'-diaminotriphenylmethane, hydroquinone, and dichloroanhydride of terephthalic acid.

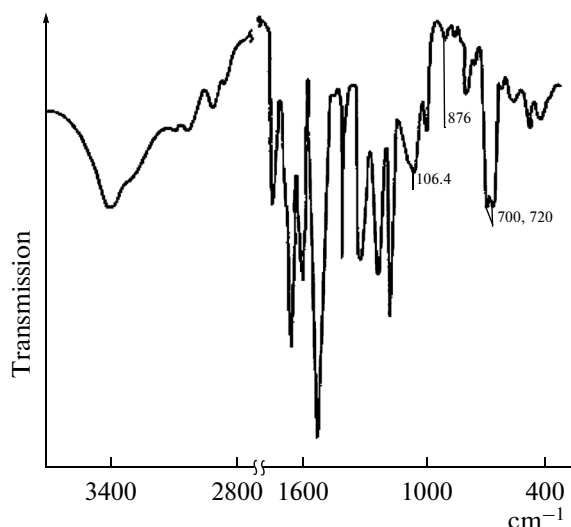


Fig. 3. IR spectrum of PAE based on 4,4'-diaminotriphenylmethane, hydroquinone, and dichloroanhydride of isophthalic acid.

isophthalic acid for preparation of PA, does not result in significant changes in the IR spectra. In the case of 4,4'-diamino-4"-methyltriphenylmethane, the disappearance of bands corresponding to monosubstituted benzene rings is observed, but as a whole the nature of the spectrum does not change.

In addition, the IR spectra of PAE were recorded. The results of analysis of the spectra of polymers based on 4,4'-diaminotriphenylmethane, dichloroanhydride of terephthalic acid, and *p*-hydroquinone revealed the presence of the following groups: monosubstituted benzene ring (bands at 700, 720, and 1172 cm^{-1}) and 1,4-disubstituted benzene ring (bands at 812, 1016, and 1408 cm^{-1}). The bands at 1508–1596 cm^{-1} correspond to vibrations of C–C valence bonds of aromatic rings, the band at 1732 cm^{-1} corresponds to ester bonds, the bands at 1636 and 1648 cm^{-1} correspond to carbonyl and amide groups, and the band with bend at 3400 cm^{-1} corresponds to an amino group; additionally, there are several bands in the region of 3032–3100 cm^{-1} corre-

sponding to valence vibrations of C–H bonds and aromatic rings (Fig. 2).

The use of dichloroanhydride of isophthalic acid changes the nature of the spectrum only insignificantly. Bands are found in the spectra (Fig. 3) that correspond to 1,3-disubstituted benzene rings (700, 876, and 1064 cm^{-1}).

Aromatic PA are of significant interest as polymers with high thermal stability [4]. However, high melting and softening temperatures, limited solubility, and significant rigidity of macromolecules interfere with processing of these polymers into products.

We produced PAE by introducing ester groups into the main chain. It was of interest to compare thermal properties of polyamides and polyamidoesters based on triarylmethane-type diamines.

Investigation of the thermal stability of PA and PAE was conducted with the help of a Q-1500 derivatograph (MOM, Hungary) using a dynamic heating mode in the temperature range of 20–600°C. The study was conducted in an inert atmosphere and in air. The heating rate was 2.5 K/min. The results of thermal analysis are presented in Table 2. As can be seen from Table 2, the PA based on 4,4'-diaminotriphenylmethane and dichloroanhydride of terephthalic acid exhibits maximum thermal stability. It was mentioned in [5, 6] that the thermal stability of PA increased in the series $m,m < m, p < p, p$, and when substituted diamines were used for PA synthesis, the thermal stability decreased slightly. Introduction of an ester group in the main chain of the macromolecule also resulted in the decrease in thermal stability.

The analysis of DTA curves makes it possible to determine the location of thermal effects related to oxidative and thermooxidative processes. The thermal effects related to oxidative processes were observed for

Table 2. Thermal properties of polyamides and polyamidoesters

Polymers	η_i , dL/g	Mass loss at temperature, °C (in air)		T_{soft} , °C
		10%	50%	
I	1.5	425	50	300
II	1.2	420	>500	290
III	1.5	415	>500	290
IV	1.3	410	>500	285
V	0.6	400	>500	265
VI	0.6	385	>500	255

the PA on DTA curves at 265°C with a maximum at 290°C. The intense mass losses corresponding to the main process of thermooxidative destruction began at 380°C (Fig. 4). The thermal effect for the PAE on DTA curves was observed at 250°C, which was related to the polymer melting. The temperature of degradation was in the range 360–450°C, which was lower than for PA. Lower thermal stability of PAE in comparison with PA is explained by the activity of the ester group in the process of heating the sample and by the lower energy of the ester bond disruption in contrast to the amide bond. The depth of transformation is much higher for PA and PAE when heating is conducted in air as compared to heating in an inert atmosphere, and the maximum weight of residue upon heating to 500°C is correspondingly lower than in an inert atmosphere.

The change in physical properties with temperature makes it possible to determine the operating temperature range of a polymer and the processing temperature range. In this connection, thermomechanical properties of the obtained polymers were investigated. The study was conducted with an UIP-70 instrument [7] in a temperature range of 20–30°C using the dilatometric mode with constant heating rate of 5°C. The results of dilatometric analysis are presented in Table 2. It can be concluded from the analysis of experimental data (see Table 2) that the softening temperature of the PA is higher than that of the PAE. The high softening temperature is explained by the availability of a large number of hydrogen bonds formed between the amide groups of neighboring molecules. As a result, a net of hydrogen bonds is formed that penetrates the entire PA bulk, as was shown by Fuller [8]. The energy of hydrogen bonds is lower than that of the main valence bonds (N–C, C–C); however, owing to their large number in each macromolecule, the total energy of interaction can be substantial.

Introduction of an ester group into the main chain of PA results in the decrease in melting temperature of the polymer. It is likely that the decrease occurs because of the increase in flexibility of the macromolecular chain, i.e., the ester groups play the role of ball joints.

The decrease in softening temperature is observed for the PA and PAE in the case where isophthalic acid is used rather than terephthalic acid (see Table 2). This is related to the fact that, unlike poly-*p*-phenylene-terephthalamide, the aromatic PA with *m*-phenylene groups have “fiber-like” location of phenylene cycles [6]. The benzene cycles are located along the fiber at alternating angles of 10° and 20° to the axis. The amide groups are placed almost perpendicularly to the plane of benzene rings, rotation of which assures low symmetry of aromatic *m*-polyamides and, hence, insignificant ordering, enhanced solubility, and decreased softening temperature.

As was mentioned above, the PAE based on 4,4'-diaminotriphenylmethane, dichloroanhydride of terephthalic acid, and hydroquinone is a partially

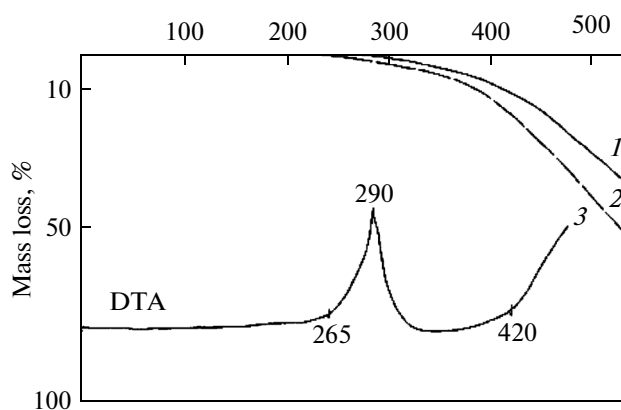


Fig. 4. Dynamic thermogravimetric analysis of PA based on 4,4'-diaminotriphenylmethane and dichloroanhydride of terephthalic acid (1) and PAE based on 4,4'-diaminotriphenylmethane, hydroquinone, and dichloroanhydride of terephthalic acid (2) and DTA (3).

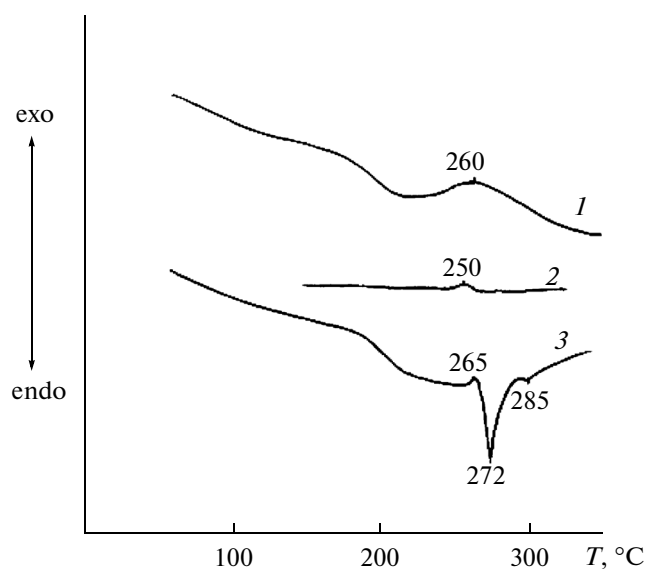


Fig. 5. DSC of PAE based on 4,4'-diaminotriphenylmethane, hydroquinone, and dichloroanhydride of terephthalic acid: (1) first heating of the sample; (2) cooling after first heating; (3) second heating.

crystalline polymer (the degree of crystallinity is around 35%) with $T_{\text{melt}} = 265^\circ\text{C}$. Phase transitions were discovered using methods of differential scanning calorimetry (DSC), dilatometry, and optical microscopy. Observation of this polymer under a polarized light microscope with heated stage reveals that the polymer melts at 270°C, displaying properties of thermotropic liquid crystals. The polymer melt displays a nematic liquid crystal state.

Investigation of polymers with the help of differential scanning calorimetry (DSC) was conducted with a Mettler instrument at a heating rate of 8 K/min) showed that an exothermic effect was observed at

260°C during heating of the sample based on 4,4'-diaminotriphenylmethane, dichloroanhydride of terephthalic acid, and hydroquinone (Fig. 5, curve 1) related to crystallization of the polymer, followed by its athermal melting. An endothermic effect at 265°C was observed in the second heating cycle following cooling (cooling rate was 5 K/min) (see Fig. 4, curve 3).

The isotropization temperature (T_i) determined with the help of DSC thermograms is 285°C. Visual observations of PAE under a polarizing light microscope did not allow accurate determination of T_i because the polymer acquired a brownish black color. This area increased in size. The results of DTA (see above) showed that the polymer based on 4,4'-diaminotriphenylmethane, dichloroanhydride of terephthalic acid, and hydroquinone lost 5% of its weight in the region of 290–350°C. The isotropization temperature of PAE coincides with the degradation temperature and does not represent a thermodynamically controlled phase equilibrium. The bend observed on the thermograms (see Fig. 5, curves 1, 3) is related to the process of devitrification of PAE at 195°C.

Observations of PAE based on dichloroanhydride of isophthalic acid under a polarizing light microscope showed that the polymer melted at 255°C and did not exhibit liquid crystal properties. This is related to the hindered segment rotation of the macromolecule chain. This is exactly what explains low melting temperatures of PAE based on dichloroanhydride of isophthalic acid. Hence, introduction of a nonlinear *para-meta* unit into the chain results in reduction of density of the chain packing of macromolecules.

In conclusion, aromatic polyamides and polyamidoesters with triarylmethane fragments in the main chain were prepared. The obtained polymers are easy to process from solution and melt. It was found that the synthesized polymers demonstrate enhanced thermal stability; the films based on polyamides display high strength indicators. It was shown that the polyamidoester based on dichloroanhydride of terephthalic acid melts, exhibiting liquid crystal properties in the temperature range of 270–285°C.

ACKNOWLEDGMENTS

This work was supported by the Ministry of Education and Science of the Russian Federation, state grant 2199.

REFERENCES

1. Hsiao S.-H., Liou G.-S., Kung Y.-C., Pan, H.-Y. and Kuo, C.-H., Electroactive aromatic polyamides and polyimides with adamantylphenoxy-substituted triphenylamine units, *Eur. Polym. J.*, 2009, vol. 45 (8), pp. 2234–2248.
2. Yu, G., Li, B., Liu, J., Wu, S., Tan, H., Pan, C., and Jian, X., Novel thermally stable and organosoluble aromatic polyamides with main chain phenyl – 1,3,5-triazine moieties, *Polym. Degrad. Stab.*, 2012, vol. 97 (9), pp. 1807–1814.
3. Hsiao S.-H. and Chang, Y.-H., New soluble aromatic polyamides containing ether linkages and laterally attached p-terphenyls, *Eur. Polym. J.*, 2004, vol. 40 (8), pp. 1749–1757.
4. Hsiao, S.-H., Chang, Y.-M., Chen, H.-W., and Liou, G.-S., Novel aromatic polyamides and polyimides functionalized with 4-tert-butyltriphenylamine groups, *J. Polym. Sci. A.*, 2006 vol. 44 (15), pp. 579–4592.
5. Byuler, K.Ts., *Teplo- i termoistoikie polimery* (Heat- and Thermal-Resistant Polymers), Vygodskii, Ya.S., Ed., Moscow: Khimiya, 1984.
6. Korshak, V.V., *Khimicheskoe stroenie i temperaturnye kharakteristiki polimerov* (Chemical Structure and Temperature Characteristics of Polymers), Moscow: Nauka, 1970.
7. Teitel'baum, V.Ya., *Termicheskii analiz polimerov* (Thermal Analysis of Polymers), Moscow: Nauka, 1979.
8. Fuller, C.S., Baker, W.O., and Pape, N.R., Crystalline behavior of linear polyamides. Effect of heat treatment, *J. Am. Chem. Soc.*, 1940, vol. 62, pp. 3276–3278.

Translated by L. Brovko