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Synthesis and Properties of Chloro-Containing Polyimides

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Abstract—A number of soluble chloro-containing (co)polyimides are synthesized by the one-step high-temperature polycondensation in *m*-cresol. The obtained (co)polymers are characterized by high heat resistance and thermal stability: 285–350 and 515–565°C, respectively. It is shown that these (co)polymers containing chlorine atoms in benzene rings and hexafluoropropylidene and cardo groups are soluble in a number of common organic solvents and form with light wavelength up to 440 nm transparent films with high stress–strain characteristics.

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Aromatic polyimides (PIs) are widely used in various fields of modern engineering as varnishes, fibers, films, coatings, and other materials, first of all, owing to their high thermal stability and ability to sustain mechanical loads in aggressive media under high temperature differentials and elevated background radiation [1–4].

Some basic technical requirements on polyimide materials often play the decisive role in the formulation of particular tasks and substantially restrict the field of their potential applications. One of these requirements, along with enhanced thermal stability, is optical transparency, which is especially important for modern electronic communication facilities, smart glasses, optical sensors, and other high-tech devices [5].

A substantial drawback of most commercially available polyimides is their poor solubility in organic solvents, which complicates their processing. Therefore, searching for new methods for the synthesis of thermally stable soluble polyimides with high tensile characteristics and optical transparency is still fairly topical.

Variations in the chemical structure of monomers in polycondensation reactions make it possible to obtain new polyimides with required, sometimes unique, properties. In order to improve the solubility of aromatic PIs, cardo groups [6–9], other bulky substituents, and flexible bridge fragments [5, 10] are introduced.

The incorporation of fluorine atoms into polyimide macromolecules improve also the solubility of polymers in organic solvents [10, 11], while preserving a high level of thermal and mechanical characteristics [12] and decreasing colorability of polymer films [4, 5].

In recent years, elevated interest has been expressed in chloro-containing polyimides demonstrating, as their well-studied fluoro-containing analogs, specific, often unique properties, in addition to a low cost of the initial components. To date, systematic investigations into the effect of chlorine substituents on the chemical and mechanical properties of polyimides are not available. Only a few papers considering the synthesis and properties of such polymers have been published [13–15].

Transparent polyimide films with a high refractive index and good thermal stability and mechanical resistance were synthesized [13, 14] by the polycyclocondensation of di- and tetrachloro-substituted benzidine with dianhydrides of various tetracarboxylic acids. In accordance with [13, 14], the colorlessness and a high optical transparency of the obtained polyimides are due to the efficient suppression of intra- and intermolecular charge transfers [14] and the prevention of dense packing of polymer chains [13]. The refractive index of chlorinated aromatic PIs is as high as 1.702–1.732. This value is extraordinarily high for the colorless PI [13]. In the authors' opinion, this phenomenon is caused by a high polarizability of chlorine atom and a bulky molecular structure of chlorinated PIs.

The investigations considered above were based on the two-step method of the synthesis of PIs which is in wide use in industry and makes it possible to synthesize high-molecular-mass soluble poly(amic acids) (PAAs). The main drawbacks of this method are the hydrolytic instability of PAAs even at moderate temperatures, the release of water upon their imidization and low molecular masses of the final polymers as a rule.

The one-step high-temperature solution polycondensation is different from the two-step synthesis of polyimides. The simplicity of one-step polycyclization, its good reproducibility, and the possibility to obtain high-molecular-mass polyimides containing almost no defective *o*-carboxyamide units make it possible to consider that this method shows promise for the synthesis of a wide variety of soluble and/or thermoplastic polyimides.

The aim of the present paper is to investigate the synthesis of chloro-containing homo- and (co)polyimides by the one-step high-temperature solution polycondensation and to study the properties of the obtained polymers.

EXPERIMENTAL

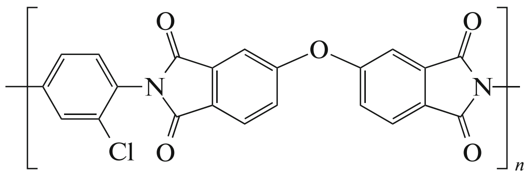
Initial Compounds

2-Chloro-1,4-diaminobenzene (T_m = 65–67/62–66°C (here and below, the values of T_m in the denominator are taken from [16])), 2,5-dichloro-1,4- diaminobenzene (T_m = 169–170/164–166°C), 9,9-bis(4-aminophenyl)fluorene (anilinefluorene) (T_m = 236–237/237–239°C), dianhydride of 2,2-*bis*-(3,4-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (T_m = 244–245/244–247°C), and dianhydride 3,3',4,4'-tetracarboxydiphenyloxide (T_m = 229–230/225–229°C) were purified by vacuum sublimation (20 Pa) at a temperature close to their melting temperature.

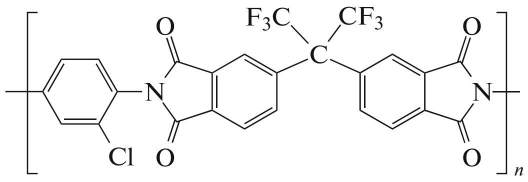
m-Cresol was distilled in vacuum in a flow of dry argon (T_b = 100°C/10 mmHg). DMF, *N*-methyl-2-pyrrolidone (MP), and chloroform were used without additional purification.

Synthesis of Polyimides

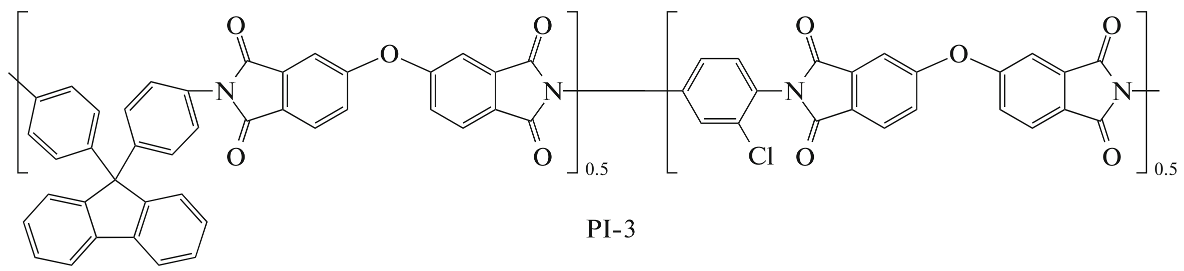
Polyimides were obtained with a quantitative yield via the one-step high-temperature polycondensation in *m*-cresol in the presence of benzoic acid as a catalyst according to the known procedure [7].



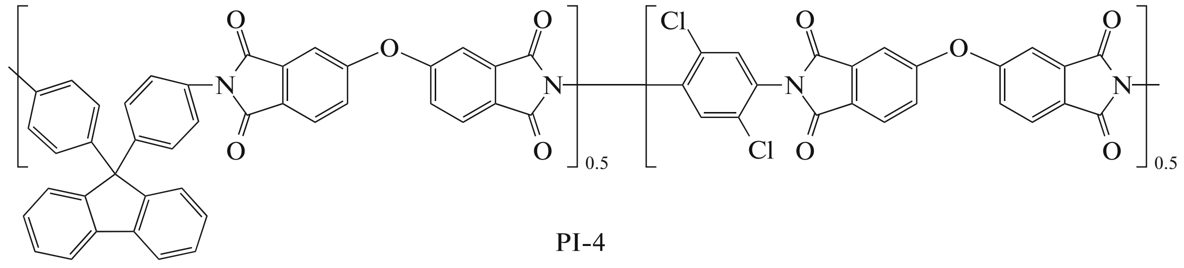
PI-1



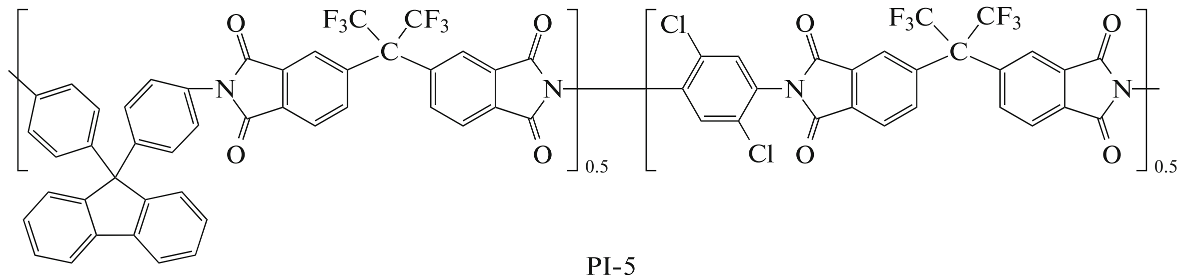
PI-2



PI-3



PI-4



PI-5

Table 1. Some characteristics of chloro-containing (co)polyimides

Polymer	Reaction time, h	η_{inh}, (MP) dL/g	Solubility		
			MP	DMF	Chloroform
PI-1	6	0.25*	–	–	–
PI-2	6	0.28	+	+	+
	17	0.70			
PI-3	6	0.90	+	+	–
PI-4	9	0.30	+	+	+
	17	0.64			
PI-5	6	0.21	+	+	+
	17	0.43			

*In H_2SO_4.

The data of elemental analysis of the synthesized polymers correspond to calculated values for PI-1–PI-5.

Analytic Methods

The inherent viscosity η_{inh} of polymer (0.05 g) solutions in the solvent (10 mL) was determined at 25°C using an Ostwald viscometer.

IR spectra were recorded on a BRUKER Tensor 37 spectrometer for sample pellets pressed with KBr.

Polymer films were cast from DMF or chloroform solutions on glass or cellophane substrates, respectively. Films with a thickness of ~30 μm were vacuum dried at 80°C.

The thermal stability of the polymers was determined by dynamic thermogravimetric analysis in air at a heating rate of 5 K/min on a Q1500 derivatograph (MOM, Hungary) using ~15-mg samples.

Thermomechanical curves were recorded on a TA Instruments TMA Q400 device (probe diameter of 2.54 mm, load of 1 N (100 g), and heating rate of 5 K/min).

Physico-mechanical tests of the films were carried out on a Polanyi-type dynamometer.

The optical transmission of the films was measured on a PerkinElmer Lambda 900 spectrophotometer.

RESULTS AND DISCUSSION

Chloro-containing (co)polyimides of different structures were synthesized from 2-chloro-1,4-diaminobenzene and 2,5-dichloro-1,4-diaminobenzene by one-step high-temperature polycondensation in *m*-cresol medium.

During the interaction of 2-chloro-1,4-diaminobenzene with dianhydride of 3,3',4,4'-tetracarboxydiphenyloxide, the forming homoPI-1 (η_{inh} = 0.25 dL/g (H_2SO_4)) precipitated even at the initial stage of synthesis. The solubility of chloro-containing PI-1 was improved and its molecular mass was increased using two approaches: the introduction of a hexafluoropropylidene group into the anhydride fragment and the synthesis of cardo polyimides with the use of anilinofluorene as a comonomer.

Both approaches proved to be useful for the synthesis of PI-2 and PI-3 (Table 1). In this case, the polymers preserved solubility in the reaction medium over the whole reaction time and possessed high molecular masses (η_{inh} = 0.70 (PI-2) and 0.90 dL/g (PI-3)). Organosoluble polyimides PI-4 and PI-5 containing 2,5-dichloro-1,4-diaminobenzene residues (η_{inh} = 0.64 and 0.43 dL/g, respectively) (Table 1) were synthesized under similar conditions but at a much longer polycondensation time (17 h).

A decrease in the rate of polycondensation for these mono- and dichloro-containing *p*-phenylenediamine derivatives is obviously due to steric factors enhanced upon the introduction of two chlorine atoms into *ortho* positions to NH_2 groups and a reduced basicity of these diamines.

The structures of the synthesized polyimides are studied by IR spectroscopy. The IR spectra of the polymers show the characteristic bands of polyimides at 1760 and 1710 cm^{-1} corresponding to symmetric and antisymmetric vibrations of carbonyl groups of imide cycles as well as bands in the range of 1380 and 720 cm^{-1} corresponding to the N–C bonds of imide cycles.

The important characteristics determining the temperature interval of performance of polymer materials are their heat resistance and thermal stability. Using TMA and TGA methods, the glass-transition temperatures and the onset temperatures of the thermo-oxidative destruction of the obtained (co)polymers were estimated. The majority of the synthesized PIs are characterized by glass-transition temperatures above 300°C (Table 2). A relatively low heat resistance of PI-1 (T_g = 285°C) may be explained by its low molecular mass (η_{inh} = 0.25 dL/g). It follows

Table 2. Thermal properties of (co)polyimides

Polymer	T_g, °C	$T_{5\%}$, °C	$T_{10\%}$, °C
PI-1	285	550	565
PI-2	320	515	530
PI-3	335	535	555
PI-4	315	540	560
PI-5	350	520	530

Table 3. Mechanical characteristics of films

Polymer	Strength at break σ, MPa	Elongation at break ε, %	Young's modulus *E*, GPa
PI-2	98	7	1.5
PI-3	86	6	2.2
PI-4	91	8	–
PI-5	87	5	2.4

Films based on PI-2, PI-4, and PI-5 are cast from solutions in chloroform; the PI-3 film is cast from DMF solution.

from the thermomechanical testing of polymers that the synthesized (co)polymers have close glass-transition temperatures (315–350°C) (Table 2), regardless of the chloro-substituted diamine structure.

In Fig. 1, the TGA curves of the synthesized polyimides are presented. It is seen that the character of these curves is the same for all of the polyimides. The temperatures of 5% and 10% weight losses lie in the range of 515–565°C. As is seen, the presence of hexafluoropropylidene groups in PI-2 and PI-5 leads to a noticeable decrease in the thermal stability of the polymers (up to 35°C).

The solubility of the obtained (co)polyimides made it possible to cast films from their solutions. In contrast to copolyimide PI-4 based on the dichloro-containing *p*-phenylenediamine, a structurally similar copolymer PI-3 containing monochloro-substituted phenylene fragments does not dissolve in chloroform. This may be due to a higher molecular mass of the latter. Close colorless flexible films with high tensile strength (1.6–2.4 GPa) and elastic modulus (86–98 MPa) were prepared from high-molecular-mass polyimides (Table 3).

In the present work, the optical properties of the most transparent Cl- and F-containing films of PI-2 and PI-5 were also investigated. As follows from Fig. 2, both films are characterized by a marked decrease in transmission at a wavelength of ≤440 nm (83 and 75% for PI-2 and PI-5, respectively). The results of optical studies for the film of polyimide based on anilinefluorene and dianhydride of 2,2-bis(3',4'-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (curve *3*) and the PI film (curve *4*) are shown for comparison. As is seen from Fig. 2, the optical transparency of the films of fluorinated and chlorinated (co)polyimides is much higher compared with the film of the commercially available PI. Comparison of the results obtained for chlorinated (curves *1* and *2*) and nonchlorinated analogs (curve *3*) indicates that the introduction of mono- or dichloro-phenylene fragments into the polymer structure promotes formation

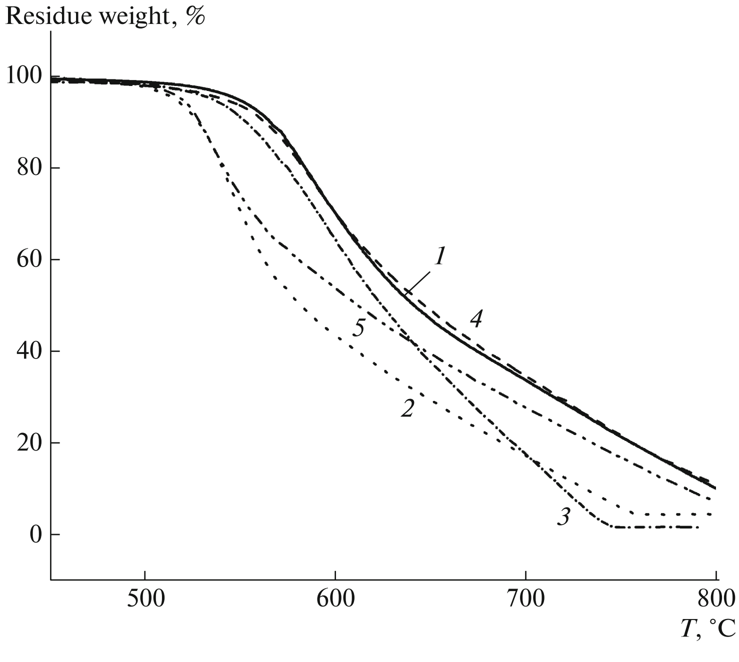


Fig. 1. TGA of (*1*) PI-1, (*2*) PI-2, (*3*) PI-3, (*4*) PI-4, and (*5*) PI-5 in air.

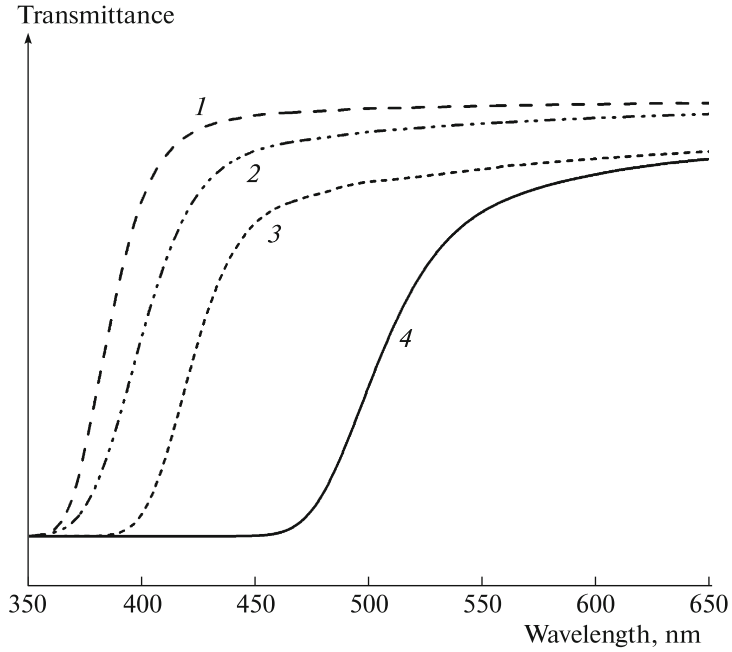


Fig. 2. Wavelength dependence of optical transmittance of (*1*) PI-1 and (*2*) PI-5 films, (*3*) the film of PI based on 9,9-bis(4-aminophenyl)fluorene and dianhydride of 2,2-bis(3,4'-dicarboxyphenyl)-1,1,1,3,3,3-hexafluoropropane, and (*4*) PI film (as a reference).

of films with improved optical transparency. These data are in agreement with the properties of polyimides containing chlorinated benzidine residues [13, 14].

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