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NEW POLYIMIDES: SYNTHESIS, PROPERTIES AND POTENTIAL APPLICATION

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Abstract

The problem of production of new materials based on polyheteroarylenes and other polymers combining good mechanical and dielectric properties, radiation and chemical stability with heat- and thermal stability is related with the development of efficient synthesis technique of starting low-molecular compounds. Alicyclic dianhydrides are believed to be the promising monomers to synthesize various polymers.

The Institute of Chemical Sciences under Kazakh Academy of Sciences has been carrying out a research for the synthesis of such dianhydrides by the photochemical method. The use of cheap and available compounds, viz. benzene, its alkyl, aryl and halogen substitutes, furan and maleic anhydride subject to ultraviolet irradiation resulted in a single stage quantitative yield of about 40 new alicyclic dianhydrides.

Various mercury-quartz lamps that may be successfully replaced by solar energy are used as an ultraviolet irradiation source.

In present years the application of nontraditional energy sources such as solar energy is rapidly emerging and promising fields.

Different polyimide materials with a complex of valuable properties were obtained on the base of alicyclic dianhydrides and various diamines. They are as follows: polyimide films, enamel insulation, molding materials.

Usually polyimides of alicyclic structure are obtained by a traditional two-step or one-step high temperature method in high boiling solvents of phenolic type. However, the polyimides obtained under conditions of two-step polycondencation are characterized by low molecular mass values due to relatively low reactivity of the initial dianhydrides. The necessity of the use of solvents of phenolic type under high temperature conditions for analysis was used. Polyimides (PI) were obtained by interaction of equimolar amounts of AB, and DADPhO in amide solvent upon the concentration of initial monomers of 40% by weight, the temperature of 120^0C, in presence of 5% by weight of carboxylic acid .

Viscosity of 0.5% solutions was determined in Ubbelohde viscosimeter at 20^0C. The cyclization process was controlled by the method described in work [4].

Thermogravimetric analysis of polymers was carried out in a derivatograph Q-1500D (Hungary). The study of physico-mechanical and dielectric characteristics were conducted on film samples with the thickness of 35-40 μm. The samples were obtained by pouring of 25% polymer solutions into DMAA on a degreased glass plate with the following drying in vacuum in the temperature range of $100\text{-}180^0$ C for 0.3 h, and they were tested for 25^0 C.

Results and Discussion

The process of PI formation under conditions of catalytic polycondencation was most influenced by the concentration of catalyst and monomers, the temperature and duration of the process, the solvent nature. Therefore, the dependency of the reduced viscosity of the polymer formed in the course of the reaction on the above said properties was studied. The reduced viscosity of the 0.5% polymer solution in DMFA was assumed as the parameter of the process optimization.

The optimum concentration of benzoic acid (as well as of pyromellitic one) is equal to 5% by weight, the polymer viscosity attains 1.82 dL/g. The further increase in the amount of benzoic acid leads to lowering of the η red values. The observed dependency of the MM synthesized polymer on the concentration of benzoic acid can be explained by two reasons. Firstly, apart from the molecular compound of amine and acid, which reacts with dianhydride at the same rate approximately as a free base [5], an inactive ionic salt of the type of $[HN\text{-}R\text{-}NH]^{+}$ ^{-}OOC [6] forms in the solvent with the increase in the concentration of benzoic acid, which results in a disturbance of the obtained in the named solvents, constituted 90 %. The full completion of the cyclodehydration reaction took place upon on additional thermal treatment of the polymer in the temperature range of 100-180^0 C for 0.3 h or at 100-120^0 C for longer time.

Elastic films with tensile strength of 170 MPa and 25-30% elongation were obtained from the reactive solutions. Their electric characteristics were studied. The table presents electrophysical parameters of a polyimide film of (35-40) 10^{-3} m thickness.Polymer varnish, obtained in the presence of carboxylic acids, is characterized by stability - it can be stored for 2 years without changing the dielectric parameters shown in the Table in the temperature range of -30- +30^0 C and it possesses good enameling ability. At present, experimental- industrial lots of wire have been produced. Polyimidic insulation possesses temperature exploitation range -100-+300^{0}C without significant changing of properties.

Thus, in the presence of catalytic amounts of carboxylic acids from dianhydrides of alicyclic tetracarboxylic acids complicates in its turn the technology of polymer production. That is why the development of simpler and more technological synthesis methods, the use of non-phenolic (amidec) solvents and search for the obtaining of polyimides in one step, constitute a very interesting task. As the conducted studies have shown, this task can be solved while using different catalysts namely carboxylic acids in the polyimide synthesis [1,2]. The studies have been conducted by the example of dianhydride of tricyclodecentetra-carboxylic acid (a photoadduct of benzene and maleic anhydride) and 4,4'-diaminodiphenyl oxide (DADPhO) in the presence of catalytic amounts of benzoic and pyromellitic acids.

Experimental

Dianhydrides of tricyclodecen-tetracarboxylic acid (AB) was synthesized by the described method by means of photochemical reaction of benzene with maleic anhydride under effect of solar energy or mercury-quartz lamps [3].

DADPhO purified by sublimation in vacuum had a melting point of 186 - 188^{0}C. The solvents: N,N-dimethylacetamide (DMAA), N,N-dimethylformamide (DMFA), N-methyl-2-pyrrolidone (MP) were kept for 24 hours above calcium hydride, then it was twice distilled in vacuum. Benzoic acid pure

equimolar ratio of the monomer functional groups. This can be confirmed by the fact that the use of strong carboxylic acids (for instance, trichloroacetic acid in the same amount as benzoic one), which form with aromatic amines a salt of ionic type, does not lead to the formation of high molecular products. Secondly, after attaining of a certain catalyst concentration in the solution a gradual isolation of the polymer from the solution occurs during synthesis due to deterioration of the solubility of the solvent, which results also in lowering of MM.

The optimum monomer concentration in the solution is 40% by weight. An increase in the concentration up to 50% by weight results in some decrease in MM polyimide, which can be stipulated by a significant increase in the solution viscosity and difficulty of mixing.

It is interesting to note the temperature effect upon the one-step synthesis of alicyclic polyimides in amide solvents. Upon a temperature increase from 90 up to 120^0 C, a considerable increase in the polymer viscosity from 1.3 up to 1.8 dL/g is observed. In this temperature range the synthesis proceeds under homogeneous conditions. Upon a temperature increase up to 130-140^0 C, the polymer precipitates.

The optimum synthesis duration at 120^0 C is 7-7.5 hours in case of benzoic acid, and 5.5 h in case of pyromellitic acid. IR-spectra of the polymer samples precipitated during the synthesis process are characterized by the presence of the absorption bands, characteristic both for the amidoacidic fragments and for the imidic ones (1670,1380,1720,1780 cm^{-1}). IR-spectrum of the resulting polymer corresponds to the polyimide structure. Amidoacidic absorption bands (1670 cm^{-1}) are absent.

As it was said above, amide solvents, such as DMAA, DMFA, MP were used as medium. More high-molecular polymers were obtained when the reaction was conducted in DMAA.

Characteristic viscosity of the PI, obtained in DMAA constituted 1.7; in MP-1.4; in DMFA-1.2 dL/g. The reactive solution remained homogeneous throughout the process. The imidization degree of PI, and diamines in amide solvents it is possible to obtain in one-step polyimides with high values of imidization, physico-mechanical and dielectric characteristics, which allows to recommend them as electroinsulating materials for different fields of technics.

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Table

Some Electrophysical, Thermal and Mechanical Parameters of the Polyimide, Based on Benzene Adduct and 4,4'-diaminophenyl Oxide

Characteristics	Values
1. Electrophysical Characteristics:	
Volume resistively, Ohm cm	
20^0 C	(1-3) 10^{16}
200^0 C	(3-4) 10^{15}
250^0 C	(2-4) 10^{14}
Dielectric loss factor (1kHz)	
20^0 C	0.001-0.003
200^0 C	0.003-0.005
250^0 C	0.005-0.007
Dielectric constant	
20^0 C	1.0 - 1.1
200^0 C	1.4 - 1.5
250^0 C	1.6 - 1.7
Dielectric strength, kV/mm	from150 to250
2. Mechanical Characteristics:	
Tensile Strength, MPa (25^0C)	150 - 180
Elongation, % (25^0C)	25 - 40
3. Thermal Characteristics:	
Initial Decomposition Temperature in Air, ^{0}C	380
Temperature of 50% weight loss, ^{0}C	580