Some Peculiarities of Creation of Stable Polyimide - Azo Chromophore System

S.K. Kudaikulova[1]*, G.I.Boiko[1], I.I.Shalabaeva[1], B.A. Zhubanov[1], M.J.M. Abadie[2]

[1]Institute of Chemical Sciences of Academy of Sciences, 106 Valihanov, 480100 Almaty, Kazakhstan
[2]Montpellier University 2. S.T.L. 340095 Montpellier CDX 5 France

Abstract

Azo dyes: methyl orange, methyl red, congo red have been suggested as doping agents for formulation of stable soluble azo dye - polyimide (PI) system according to guest-host scheme. The dyes were added to the reactive mixture of monomers: dianhydrides of alicyclic tetracarboxylic acids and aromatic diamines. Polyimide synthesis was carried out by one step polycyclocondensation in protolytic media. Addition of azo dyes influences on the molecular weights of final PIs. In great extent they depend on the nature and concentration of doping agent. Investigation of dependence of reduced viscosity of PI on monomers concentration, duration and temperature of synthesis, concentration of doping agent. It has been determined that addition of dyes to the reaction mixture up to definite value rises molecular weights of PIs from 45-50 000 up to 320-330 000. The most efficient catalyst is congo red. However some functional groups of azo dyes disturb equimolarity of the reaction by interaction with one of main monomers. The colour of thus doped PIs is stable under processing and high temperatures. Stability of the azo dye - polyimide system depends on interaction of NLO agent with polyimide chain. It is suggested that congo red molecules can coordinate with carbonyl groups of polymer. PI films display solvatochromic properties.

Introduction

During last few years the works on design of materials with specific properties attract great attention. Creation of polymer-chromophore system allows to obtain polymers with nonlinear optical (NLO) properties. Usefulness of these doped polymer systems in integrated optical devices as well as solvatochromic applications depends on physical and chemical stability of the system. Creation of such materials on the basis of polyimides (PI) is actual because of their high thermal, radiaton, chemical stabilty along with their ability to form strong thin films. However the main problem of creation of azo doped PI materials is connected with low solubility of PIs and full decomposition or sublimation of the chromophoric part of the system at high temperatures.

Elaboration of the ways to avoid these problems includes in creation of guest-host systems [1-3], synthesis of dianhydrides containing azo group in main chain [4], full functionalizing of diamines with side chromophoric groups [5-7]. In our previous works [8] we have shown that addition of azobenzene is similar to the effect of other organic bases (tertiary amines, amides) [9] and leads to increase of molecular weights of synthesized PIs. From the regard of creation of stable azo dye - PI guest-host system it is suggested to add azo dyes which satisfy to the condition of nonlinearity of optical properties, into the reactive mixture of monomers. NLO chromophores are usually comprised of strong electron donor and acceptor groups connected by π-conjugated unit. Multifunctional nature of these compounds effects on the process of PI formation and stability of whole azo dye-PI.

Here we represent the results on synthesis of alicyclic PIs in the presence of special conjugated azo compounds which allow to obtain stable azo dye doped PIs with solvatochromic properties and as promising materials for nonlinear optic application.

Experimental

Materials

Anhydrides of alicyclic tetracarboxylic acids have been obtained in the Laboratory of polymer synthesis of the Institute of Chemical Sciences, Kazakhstan.

*corresponding authors. E-mail: ics-rk@hotmail.com

They were synthesized according to the reaction of Diels-Alder by reaction of benzene or toluene with maleic anhydride in the presence of acetophenone as sensitizer of UV-irradiation in excess of the first component[10,11]. Thus obtained dianhydrides were washed with hot acetone several times. Then the dianhydrides were boiled with 1,5% excess of acetic anhydride, washed with diethyl ether and dried at 100°C and vacuo up to the constant weight. Cleaned dinhydrides were sublimated.

Dianhydride of thricyclo[-(4,2,2,0)^{2,5}-dec-7-en-3,4,9,10]tetracarboxylic acid (BA adduct of benzene and maleic anhydride, $C_{14}H_{10}O_6$). Elemental analysis; calculated C 61.31; H 3.66; found C 61.11; H 3.61; M.P.: 351°C; neutralization equivalent: calculated 137.0; found 137.0, m.p.: 351°C

Maleic anhydride was recrystallized from benzene, then it was twice distilled at b.p. 199.9/690 mm Hg; m.p.: 52.0°C.

Oxydianiline (ODA) was sublimed under vacuo at 200°C /6.10^{-3} mm Hg; m.p.: 185.6°C.

Azobenzene was twicely recrystallized from 95% ethanol, m.p.: 66°C.

The dyes: congo red, naphthyl red, methyl orange, methyl red malachite green and crystall violet were recrystallized from the 95% ethanol.

The solvents: benzene, m-cresol, dimethylsulfoxide (DMSO), dimethylformamide (DMF) were purified by usual methods.

Synthesis of polyimides

PIs have been synthesized in three neck flask in one step polycondensation of dianhydride (BA or TA) with ODA in m-cresol at 170-190°C in the flow of inert gas. The final products - polyimides were poured into acetone and dried in vacuo at 100°C. The dried polymers were dissolved in DMSO or DMF to form 13-15% weight solutions. The polyimide solutions were cast on the glass plate and dried in an oven rising the temperature gradually from 100 to 180°C. After cooling obtained films were stripped off the plate.

PI films doped with congo red were immersed into 0,1 N HCl aqueous solution, washed with water, acetone and then dried in an oven.

Measurements

The reduced and intrinsic viscosities of the polymers were determined in DMSO at 20°C, concentration of the solution 0,5 dl/g, by using an Ubbelohde viscometer.

Molecular weights of polyimide samples were estimated from the intrinsic viscosity [η] measurements in DMSO solutions of the polymer applying the [η] - M_w relationship. The constants K and α were obtained for alicyclic PIs by light scattering previously [12]. The relationship is as follows: $[η] = 9,79·10^{-4}$. $M_w 0,61$; K= 9,79·10^{-4}, α=0,61.

Infrared spectra were recorded on a Specord UR-20 Spectrophotometer using KBr pellets or polymer films of 3-6 μm thickness. The spectrum is characterized by presence of the bands: ν = 1380 cm^{-1}- C-N; 1720,1780 - C=O vibrations of the imide cycle.

UV spectra of the films were recorded on a Jasco Model 750 UV/VIS spectrophotometer.

Thermogravimetric analysis (TGA) was performed on a derivatograph Q-100 (System Paulic, Paulic Erdey) MOM at a heating rate 10°C/min.

The mechanical properties - tensile strength (σ, MPa) and elongation (l,%) at 20 and 200°C were evaluated on specimens (22.10, thickness 0,03-0,05 mm).

Volume resistivity, ρ; electric break down, E; the loss tangent of a dielectric, tg δ were determined according to used methods at 20 and 200°C.

Dynamic mechanical analysis has been performed on Universal v2.F TA Instruments.

Results and discussion

Reaction of alicyclic dianhydrides with aromatic diamines was conducted by one step high temperature polycondensation according to the following scheme:
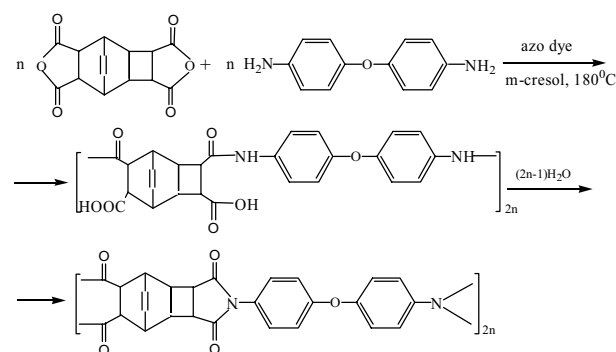
Azo compounds: congo red, methyl orange, methyl red were added to the reactive mixture of monomers. Final PIs in the form of films produced immediately from the reaction solution as well as in the form of fibers precipitated into the acetone or alcohol were coloured. PIs are soluble in aprotic solvents and their

colour depends on the dye's nature and remains stable during multiply reprecipitation.

The process of PI formation in the presence of doping agents was investigated according to the dependence of reduced viscosity (η_{red}) on main factors: monomers concentration, duration of synthesis, temperature and concentration of doping agent. In the Fig.1 there are presented the relations of η_{red} - C_{mon}. Obtained similar values of optimal monomers concentrations for PI synthesis (30 weight%) are independent on the dye's nature. This fact indicates that in this relation viscosity and diffusional factors play main role. Investigation of temperature dependence (Fig.2) have shown that PIs with highest reduced viscosities are formed in the region 175-185°C. Temperature 180°C is considered to be optimal. Temperature dependence is important from the regard of two points. Determination of optimal temperature as well as stability of azo compounds in conditions of high temperature synthesis. As it can be seen from the Fig.2 there are no sharp decreases of the viscosity in the course of the curves. This presents an evidence that these azo compounds do not undergo chemical conversions.

Recently investigation [12] of one step synthesis of PIs in presence of tertiary amines, amides of carboxylic acids has shown that they significantly
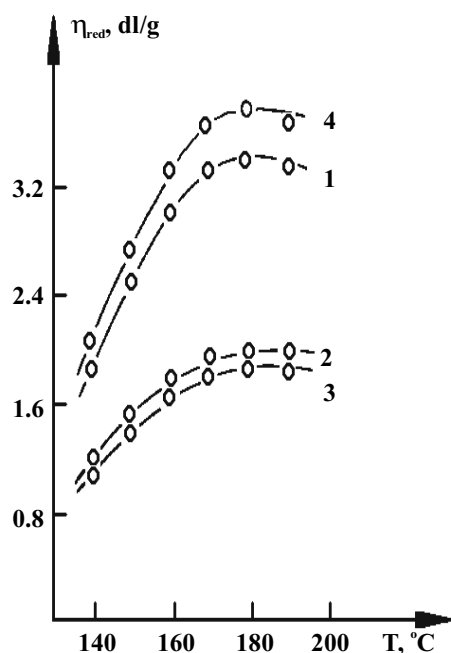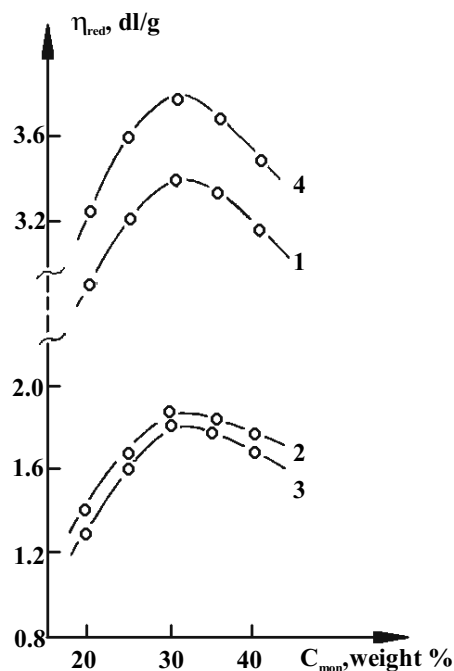

Fig.2. Dependence of reduced viscosity of PI on the basis of BA and ODA obtained in presence of congo red (1), methyl orange (2), methyl red (3) azobenzene (4) on temperature

increase the rate of molecular weights rising as well as their final values. Kinetic investigations has shown that amides accelerate both steps of PI formation: polyacylation and imidization. Taking into account these results we can suppose that increase of molecular weights of PIs in the presence of azo dyes is due to catalytic effect of these compounds. Similarly catalytic efficiency of azo dyes can be estimated according to the rate of increase of reduced viscosity and it's maximum value for the doped and undoped processes.

The curves of time dependence of reduced viscosity are presented in the Fig.3. The rate of increase of molecular weight of polymer in the course of synthesis and it's final value are higher for PI synthesis in presence of congo. It is seen that for the synthesis duration 3 hours η_{red} = 2,87 dl/g for PI/congo red (curve 1) whereas for the PI obtained without doping agent (curve 5) η_{red} = 0.59 dl/g. Similar value of η_{red} = 0,85 dl/g for the noncatalytic process is achieved during 5 hours whereas for doped process in the presence of congo red it achieves during 40 minutes. Optimal time for the reaction was taken 6 hours.

From the regard of estimation of catalyst's nature the relation between η_{red} - C_{azo} is very important. It is seen (Fig.4) that all curves have extreme character what allows to determine optimal concentration of

Fig.1. Dependence of reduced viscosity of PI on the basis of BA and ODA obtained in presence of congo red (1), methyl orange (2), methyl red (3), azobenzene (4) on monomers concentration

dye. Congo red significantly rises reduced viscosity, two others: methyl orange and methyl red display lower
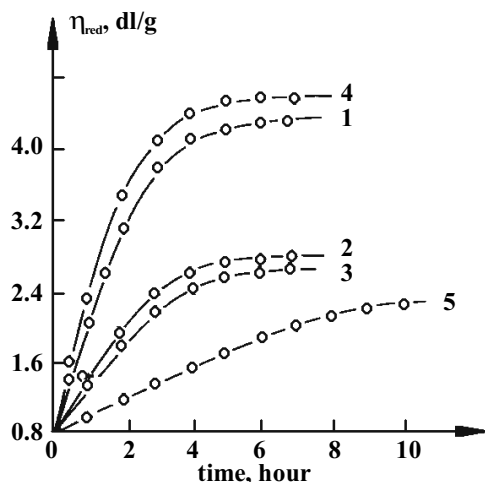

Fig.3 Dependence of reduced viscosity of PI on the basis of BA and ODA obtained in presence of congo red (1), methyl orange (2), methyl red (3) azobenzene (4) and without catalyst (5) on duration of synthesis
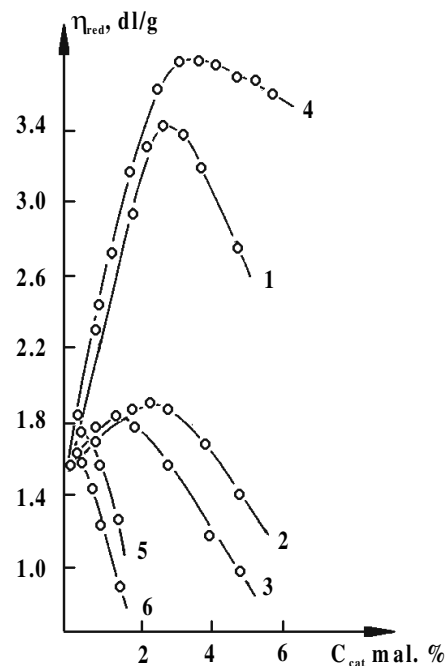

Fig.4. Dependence of reduced viscosity of PI on the basis of BA and ODA obtained in presence of congo red (1), methyl orange (2), methyl red (3), azobenzene (4), naphthyl red (5), p-amineazobenzene (6) on catalyst's concentration

activity. Reduced viscosity for PI obtained without catalyst =1,41 dl/g. Addition of 3 mol.% of congo red to the reaction mixture resulted in formation of PI with η_{red} = 3,41 dl/g. At the catalyst's concentrations higher than optimal reduced viscosity sharply decreased. Extreme character of the curves η_{red} - C_{azo} suggests that addition of azo compound gives rise to two processes: increase of molecular weight of PI possibly to catalytic effect on the polyacylation step and at concentration range higher than optimal - decrease owing to the interaction of dye's functional groups with anhydride or amine groups. Azo dyes represent themselves multifunctional compounds which contain such groups as $COOH$, SO_3H, $N(CH_3)_2$, $N=N$. Increase of molecular weights may be explained as effect of acidic [13] or basic [9] catalysis of one step formation of PIs in protolytic solvents. However interaction of dye with PI matrix along with it's negative effect presents the possibility to form stable guest-host system in the process of PI formation. Intrinsic viscosity of of PI obtained in optimal conditions $[\eta]$=2,39 dl/g what corresponds to molecular weight 340 000 according to Marc-Kun equation.

Study of influence of each functional group is necessary for the estimation of whole catalytic activity of the azo dye molecule. Lower efficiency of methyl red and methyl orange on the molecular weights can be explained by presence of acidic groups (COOH,

SOH) which probably take part in the salt formation with diamine component and it's blocking in the acylation process. Indirect evidence of this suggestion is behaviour of dyes: malachite green and crystal violet as catalysts.

They represent compounds with dimethylaniline groups and chromophoric system of another nature. Catalytic activity of these dyes is due to dimethylaniline group (η_{red} = 1,8-1,9 dl/g) and nonability to color PIs is due to absence of functional groups which are able to react with amine or anhydride groups.

Congo red has two symmetrical -NH_2 groups and it may be suggested that they are concurrent of main monomer. However up to 3 mol.% it acts as efficient catalyst. Conventional modeling of congo by the use of azobenzene, p-amineazobenzene and naphthyl red in the reaction has shown that azobenzene is the most efficient catalyst and decrease of the reduced viscosity in the region C_{cat} > 3,5 mol.% is quiet (Fig.4, curve 4). P-amineazobenzene and naphthyl red are monoamines, their addition to the reaction mixture leads to full disruption of equimolarity (Fig.4, curves 5,6), however PIs obtained in the powder form have stable colour. Low functional activity of two symmetrical -NH_2 groups of congo red as concurrent of diamine monomer is due to those fact that they take

part in highly conjugated system of whole molecule. Participation in the conjugated system leads to decrease of nucleophility of nitrogen atom and as a result - increase of acidic properties of hydrogen in amine group. This reduces reactivity of N atom in the possible reaction with carbon of anhydride group but rises his complexation ability with oxygen atoms of carbonyl C=O. Complexation of carbonyl group with congo red proceeds according to formation of hydrogen bonds and Van der Waals forces.

The UV-spectroscopic (Fig.5) data confirm that complex formation of congo red with PI matrix proceeds on the level of hydrogen bonds. The spectrum of congo doped PI has the bands at 343 and 514 nm. Spectrum of congo red in the solutions of DMSO and ethyl alcohol is characterized by two bands: $\lambda=345$ and 506 nm. Colour of PI/congo red films is stable up to decomposition begining temperature. UV spectra of the films exposed at 220°C during 6 hours remain without changes. These results give an evidence that congo red is one of optimal chromophores for NLO.
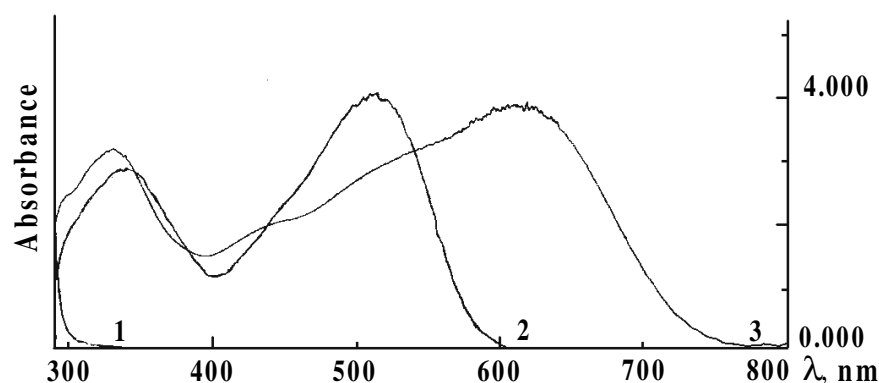

Fig.5 UV-VIS spectra of PI film on the basis of BA and ODA (1), PI film doped with congo red, congo (2) , PI/congo film treated in 0,1 N HCl solution (3).

It is known also that congo red is indicator of medium acidity. When protonation of amine group takes place conjugated system of molecule undergoes changes due to conversion of benzoid structure to chinoide one and colour transfers red $\rightarrow$ blue. The solvatochromic nature of the dyes remains in the doped films. Conversion of the color for PI/congo film «red - blue» is stable and multiply reversible Fig.5 represents spectrum of protonated PI/congo film. It is seen that band $\lambda=343$ nm shifted to $\lambda=328$ nm and the second band $\lambda=514$ nm has shifted to the region 610 nm. Solvatechromic properties of the films are stable and do not change mechanical properties of the films.

Investigation of thermal stability of PI doped with congo red has shown that initial decomposition temperature is similar to pure alicyclic PIs and remains 360°C.

The solubility of PIs in the solvents of amide type allowed to produce films on the «Hofman-Schwabe-Krefeld» machine.

Dynamic mechanical analysis of the films is presented in the Figures 6 and 7. It is well seen that according to the relations of storage modulus and loss of modulus the properties of congo doped PI films are higher.

Mechanical and electrical properties of thus obtained PI films are presented in the Table 1. As it is seen from the Table 1 PI/congo red films are characterized by improved physical properties in comparison with PI obtained without catalyst. This is due to high molecular weights of PIs obtained in the presence of catalyst. The films on the basis of PIs doped with methyl red and methyl orange displayed physical properties similar to undoped PIs.

Conclusions

Investigation of thermal characteristics has shown that independently on doping agent decomposition temperature of PI matrix keeps the same. According to the data of thermal stability alicyclic PIs can be related to the class of polyamideimides.

High molecular weights of polyimides obtained in presence of congo results in significant improving of mechanical properties of the films. Electrical proper-
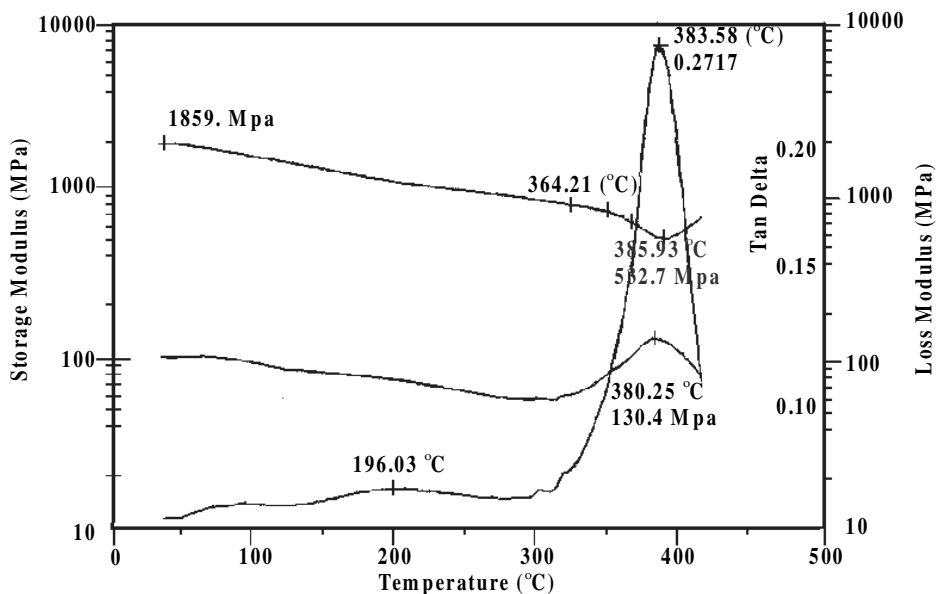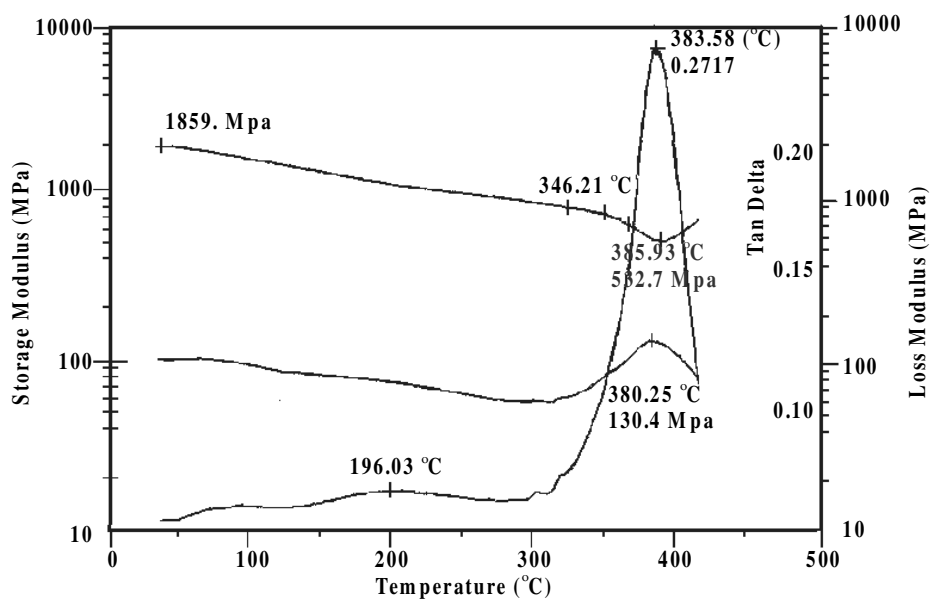
Fig.6. DMA analysis of PI film

Fig.7. DMA analysis of PI/congo doped film

Table 1.

Mechanical and electrical properties of PIs on the basis of BA and ODA at different temperatures

catalyst	η_{red}, dl/g	Testing temperature	mechanical		Electrical		
			σ, MPa	l , %	ρ, ohm·cm	tgδ at 10^3 hertz	E, kV/mm
Without	0,8	20	94	7,0	$1\cdot10^{16}$	0,003	150
catalyst		200	54	5,7	$1\cdot10^{13}$	0,007	180
congo	3,31	20	170	22	$2,8\cdot10^{16}$	0,001	200
red		200	117	28	$3,1\cdot10^{14}$	0,005	190

ties of these PIs characterize them as dielectric materials of middle frequency.

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