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CONFERENCE. AMORPHOUS, VITREOUS, AND POROUS SEMICONDUCTORS

Photosensitivity of New Photoconductive Polymers Based on Ruthenium–Biquinolyl Complexes

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Abstract—A set of new metal–polymer complexes has been synthesized on the basis of polymers containing biquinolyl units in the main chain and $Ru(bPy_2)Cl_2$. The spectral and mechanical properties of these complexes were studied, as well as their photosensitivity in the temperature range from 20 to 150°C. It was shown that the photosensitivity of synthesized polymers is 2×10^4 cm^2 J^{-1} and the quantum yield of carrier photogeneration is $\eta = 0.025$. © *2003 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

In the context of the promising application of polymer–metal complexes (the possibility of implementing new physical principles for data recording and storing; the photoconductivity, self-assembly, and self-organization of polymer structures; etc.), much attention has been given to the synthesis of new polymers which allow functionalization of polymer matrices by transition-metal ions.

From the viewpoint of various physical applications, the most attractive are metal–polymer complexes based on divalent ruthenium. They feature a unique combination of chemical stability, redox properties, luminescence, and a long lifetime of the excited state [1]. Recording materials produced on the basis of such complexes are characterized by nonlinear optical and photorefractive properties (the optical yield is 200 cm^{-1} at the field $E = 0$, the quantum efficiency is 0.2% at $E = 10^6$ V cm^{-1}, the diffraction efficiency is ~1% [2]); high resolution, which is characteristic of molecular media; high carrier mobilities (~10^{-5} cm^2/(V s) [3]); and photosensitivity (~3×10^4 cm^2/J [4]). Concerning fabrication of electroluminescence devices [3], recording media based on metal–polymer complexes have a rather high luminescence efficiency (luminous emittance) at relatively low operating potentials.

In our opinion, it is of interest to obtain metal–polymer complexes on the basis of polymer matrices, featuring high thermal stability. Such complexes are characterized by the presence of biquinolyl units in the structure of thermostable polymers. As an object of study, we took polybenzoxazinoneimides, since (as shown previously [5]) these polymers exhibit a unique combination of hydrolytic stability of prepolymers and thermal stability of corresponding products of their cyclization.

2. EXPERIMENTAL

The objects of study were soluble metal–polymer complexes **I** (see Figs. 1a, 1c) produced by the interaction between polyamide acid **II** (PAA) and $Ru(bPy_2)Cl_2$ (where bPy is 2,2'-bipyridyl) in *N*-methylpyrrolidone (the method referred to as "assembling") (see Figs. 1b, 1c).

PAA containing biquinolyl units in its main chain was synthesized on the basis of 2,2'-biquinolyl-4,4'-dicarboxylic acid dichlorides, *N*,*N*-diphenyloxide-bis-(trimethylimido) acid, and methylene-bis-anthranil acid by low-temperature polycondensation.

The synthesis of 2,2'-biquinolyl-4,4'-dicarboxylic acid was carried out using the Pfitzinger reaction from isatin and acetoin (see [6]). The synthesis of *N*,*N*-diphenyloxide-bis-(trimethylimido) acid is described in [5]. The synthesis of dicarboxylic acid dichlorides, $Ru(bPy_2)Cl_2$ complex, and PAA was performed according to the procedures described in [5], [7], and [4], respectively. PAA–$Ru(bPy_2)Cl_2$ complex was synthesized at 190°C in *N*-methyl pyrrolidone according to [8]. The polymer solutions obtained were poured onto glass substrates to form films, which were dried at 80°C up to a contrast mass. The thickness of films designed for measuring the mechanical properties and photosensitivity was 30–40 μm and 1–3 μm, respectively.

The technique for studying the photosensitive properties included measurement of the spectra of the photosensitivity $S_{0.1}$ and the quantum yield of carrier photogeneration η. The photosensitivity $S_{0.1}$ was determined by such a criterion as the reduction of the surface potential by 10% of the initial value. The measurements were carried out in the electrophotographic mode in the spectral range of 400–800 nm under electric fields of 10^4–10^6 V cm^{-1} using the technique [4]. The thermalization length r_t and the quantum yield η_0 of bound-pair formation were determined by the field-dependence slope within the Onsager model.

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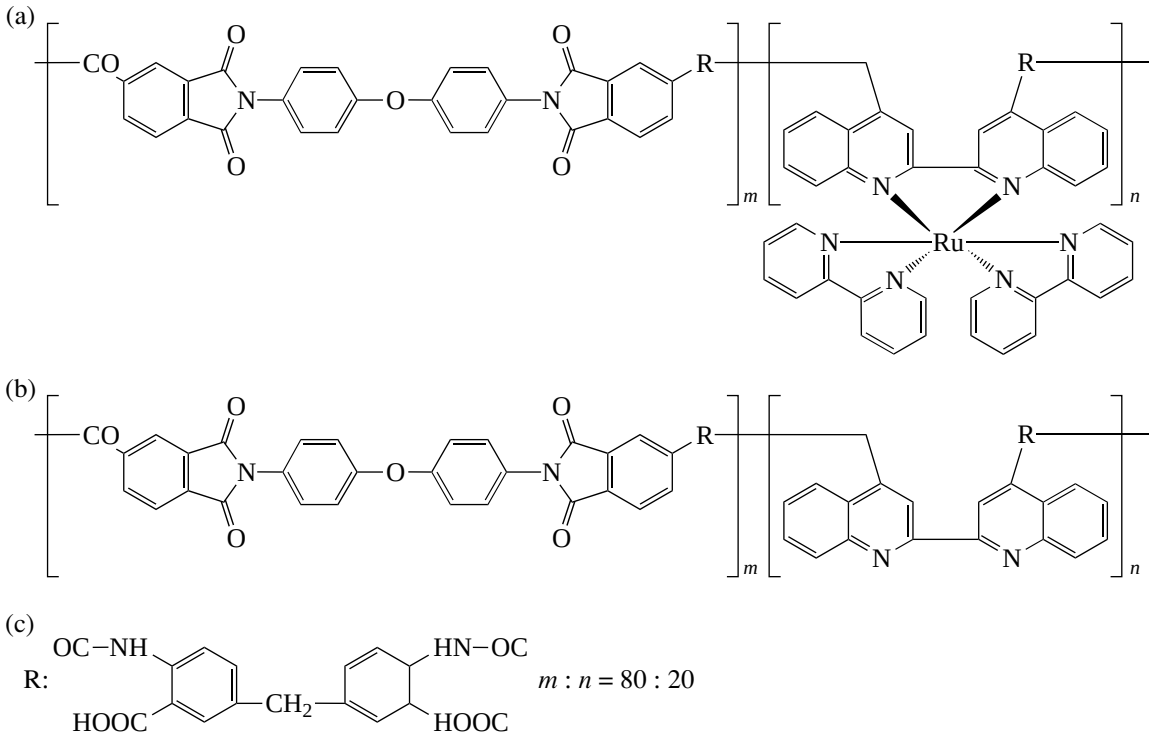

Fig. 1. (a) Metal–polymer complex **I**, (b) polyamide acid **II**, and (c) fragment *R* in Figs. 1a, 1b.

The mechanical characteristics of the films of metal–polymer complexes were measured using the technique [5].

3. RESULTS AND DISCUSSION

All of the synthesized polymers are characterized by rather good deformation–strength properties (E = 2.8–3.2 GPa, σ_p = 95–110 MPa, ε_p up to 20%). The presence of ruthenium has almost no effect on the mechanical properties of films. It is noteworthy that some decrease in the elastic modulus of metal–polymer complexes is observed, which is explained by the screening of hydrogen bonds by $Ru(bPy)_2^{2+}$ volume units.

Figure 2 shows the absorption spectra of synthesized model compounds: complexes of bivalent ruthenium with bipyridyl $Ru(bPy_2)Cl_2$, with bipyridyl and 2,2'-biquinolyl-4,4'-dicarboxylic acid (bqa) $Ru(bPy_2)Cl_2$; metal–polymer complex **I**; and the initial compounds: (bqa) and polymer **II**.

We can see from the spectra that polymer **I** (curve *4*) and bqa (curve *2*) virtually do not absorb in the range of 400–700 nm. The spectrum of the low-molecular complex $Ru(bPy_2)Cl_2$ (curve *1*) contains two intense peaks at 360 and 520 nm. The latter peak is caused by the metal-to-ligand charge transfer (referred to as MLCT [1]). The spectrum of $Ru(bPy)_2(bqa)Cl_2$ (curve *3*) has a similar shape, but its peaks are shifted to longer waves, which is caused by the influence of the biquinolyl ligand itself and its carboxyl groups. The spectrum of PAA + $Ru(bPy_2)Cl_2$ (curve *5*) exhibits a broad peak in the range of 470–560 nm, which indicates the formation of metal–polymer complex **II**.

Figure 3 shows the photosensitivity spectra of the synthesized materials. We can see that photosensitivity increases by almost an order of magnitude (curve *2*) in the case of ruthenium complex formation in comparison with the initial polymer (curve *1*) and is equal to

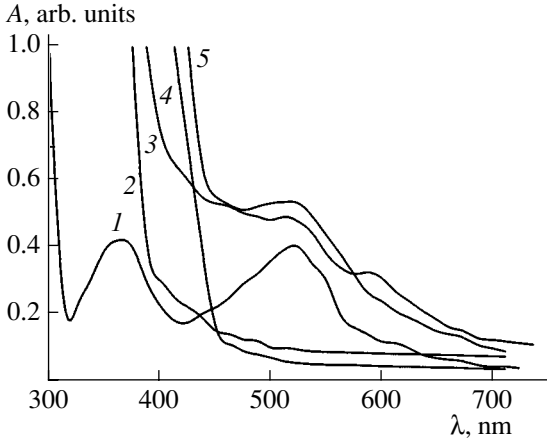

Fig. 2. Absorption spectra of the synthesized compounds: (*1*) $Ru(bPy_2)Cl_2$, (*2*) 2,2'-biquinolyl-4,4'-dicarboxylic acid (bqa), (*3*) $Ru(bPy)_2(bqa)Cl_2$, (*4*) polyamide acid (PAA), and (*5*) PAA + $Ru(bPy_2)Cl_2$.

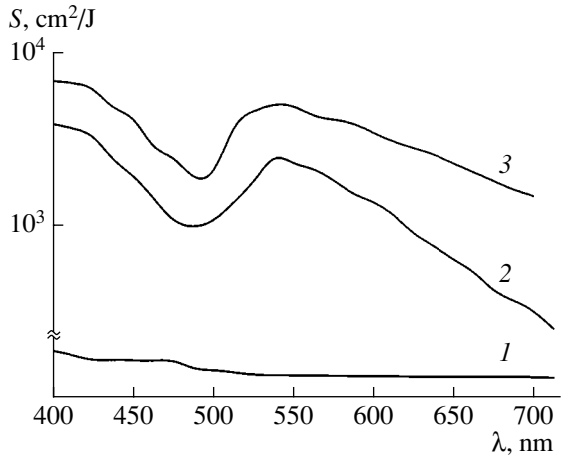

Fig. 3. Photosensitivity spectra of synthesized polymers: (*1*) PAA, (*2*) PAA + $Ru(bPy_2)Cl_2$, and (*3*) PAA + $Ru(bPy_2)Cl_2$ + fullerene.

2×10^4 cm^2 J^{-1}. In the case of incorporation of fullerene (a sensitizer increasing the electron mobility) into the metal–polymer complex, the photosensitivity further increases by a factor of 2–3 (curve *3*) in comparison with the complex without fullerene. The most significant increase is observed in the long-wave length spectral region. The quantum yield of carrier photogeneration η of the metal–polymer complex is constant within the absorption band and is equal to 0.025, which is somewhat lower than that of similar biquinolyl complexes with Cu [4]. The quantum yield of bound-pair formation is $\eta_0 = 0.06$, and the thermalization length r_t is 3.0 nm. This value is comparable to the value of r_t for complexes with copper. In the case of metal–polymer complexes with fullerene admixture, η is higher than that of complexes without fullerene by a factor of 1.5. Thermal treatment of the polymeric materials under study (heating up to 150°C) does not decrease their photosensitivity.

4. CONCLUSIONS

(i) New polyamide acids with biquinolyl units in the main chain and their complexes with $Ru(bPy_2)Cl_2$ have been synthesized. Their mechanical and physical properties were studied.

(ii) It was shown that the synthesized metal–polymer complexes are characterized by a rather high photosensitivity, which can be significantly increased by fullerene sensitization.

(iii) The developed method opens up wide opportunities for synthesizing metal–polymer complexes, which may be of practical importance for producing photoconductive systems.

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