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PHOTOPOLYMERIZATION OF SILOXANE-THIOL-ACRYLATE OLIGOMERS

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Photosensitive polymer materials are prospective for the development of optical elements in integrated and diffractive optics. For this purpose, photopolymer hybrid organic–inorganic compositions are actively developed and studied. Acrylate groups, which can undergo free-radical photopolymerization, are frequently used as monomer groups in such materials. When multifunctional acrylates are used, a cross-linked polymer is formed by the action of UV light. It is accepted that the disadvantage of free-radical photopolymerization in thin films is its inhibition by atmospheric oxygen. This inhibition results from the formation of peroxide radicals, which traps free radicals and prevent further polymerization. It is known that the use of thiol compounds in acrylate photopolymer compositions helps to eliminate the oxygen inhibition of radical polymerization. The synthesis of hybrid oligomers for photopolymer compositions was carried out based on the thiolene reaction between the tetraacrylate dihydroxydiphenylsulfide derivative and siloxane-thiol oligomer. Siloxane-thiol oligomer was synthesized by condensation of diphenylsilanediol and 3-(mercaptopropyl)-trimethoxysilane. The siloxane-thiol oligomer structure was identified by 1H, 13C, 29Si NMR spectroscopy including COSY, HSQC, and HMBC methods and by MALDI-TOF mass spectrometry. The hybrid oligomers were obtained at different tetraacrylate: siloxane-thiol oligomer ratios. The obtained compositions were resistant to the oxygen inhibition of photopolymerization and give flexible, thermostable, and rigid polymer films under UV light. The degree of the film photopolymerization was monitored by IR spectroscopy. The thermomechanical properties of photopolymer films were determined using thermogravimetric, differential scanning calorimetric, and dynamic mechanical analyses. The storage modulus (E_0) at room temperature (1.16–1.88 GPa) and the glass transition temperatures (78–133°C) were determined for photopolymer films obtained at different ratios of acrylate and thiolsiloxane units. The photocured hybrid films exhibit high stability to thermal decomposition in the inert (T10% over 321 °C) and oxidizing (T10% over 314°C) atmospheres. The kinetics of thiol–enol photopolymerization of a hybrid composition based on a tetraacrylate monomer and a thiol-siloxane oligomer was studied with the use of a holographic recording of elementary transmission phase gratings. The degrees of conversion of double bonds in the tetraacrylate monomer after the polymerization in air and in an inert atmosphere of SF6 were measured via IR spectroscopy. It is shown that the use of the thiol-siloxane oligomer efficiently suppresses oxygen inhibition of the photopolymerization. An increase in the thiol-siloxane oligomer concentration leads to an extremal dependence of the photopolymerization rate on the oligomer concentration; the maximum rate is reached at an oligomer concentration of about 0.07 mol/L. The kinetic scheme of photopolymerization in the hybrid photopolymer composition was analyzed, and an analytical expression for the photopolymerization rate was obtained. The correlation between the kinetic constants of the thiol-enol photopolymerization was evaluated on the basis of the obtained parameters of the kinetic model. The results of the laser recorded structures in the hybrimers are represented.

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Recent Publications

1. I Yu Kargapolova, N A Orlova, K D Erin and V V Shelkovnikov (2016) Synthesis of unsymmetrical thioflavylium dyes from julolidine derivatives and polyfluorinated triphenyldihydropyrazoles. Russian Journal of Organic Chemistry 52(1)37–41.
2. V V Shelkovnikov, D I Derevyanko, L V Ektova, N A Orlova, V A Loskutov, *et al.* (2016) Photopolymerization kinetics of a thiol-enol composition determined via recording/playback of a transmission holographic diffraction grating. Polymer Science Series B 58(5)519–528.
3. N G Mironnikov, V P Korolkov, D I Derevyanko, V V Shelkovnikov, O B Vitrick, *et al.* (2016) Study of optical and thermo-optical properties of a hybrid photopolymer material based on thiol-siloxane and tetraacrylate oligomer. Optoelectronics, Instrumentation and Data Processing 52(2):180–186.
4. V V Shelkovnikov, G A Lyubas and S V Korotaev (2016) Enhanced reflective interference spectra of nanoporous anodic alumina films by double electrochemical deposition of chemical metal nanoparticles. Nanoscale and Nanostructured Materials and Coatings, Protection of Metals and Physical Chemistry of Surfaces 52(2)227–231.
5. E F Pen, I A Zarubin, V V Shelkovnikov and E V Vasil'ev (2016) Method for determining the shrinkage parameters of holographic photopolymer materials. Optoelectronics, Instrumentation and Data Processing 52(1)60–69

Biography

Vladimir Shelkovnikov is Head of Laboratory of the Light-Sensitive Materials in the Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences. Education: Tomsk Polytechnical Institute, Tomsk, USSR, 1978, Chemistry, Radiation Chemistry, Chemical Technology Engineer; Kemerovo State University, Kemerovo, USSR, 1984; PhD in Physical Chemistry; Institute of Inorganic Chemistry, Novosibirsk, Russia, 2009, Degree Doctor of Science in Physical Chemistry. His field of research interests are chemistry and photonics of the organic chromophores and polymer compositions. He has more than 30 years of varied experience in chemistry and photonics of organic medium.

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