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INVESTIGATION OF THE INFLUENCE OF THE COUNTERION ON THE REFRACTIVE INDEXOF IONIC POLYMERS

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Abstract This paper is devoted to the development of polymer materials with a controlled refractive index based on polymeric analogues of ionic liquids or poly(ionic liquids) (PIL). Two series of ionic polymers with different type of counterion were synthesized and their thermal and optical properties were investigated. The refractive index (RI) of ionic polymers were calculated theoretically (by Askadskii method and by atomic additive empirical scheme Ab Initio) and was measured by ellipsometry resulting in the range from 1.40 to 2.83, and 1.44 to 2.06, respectively. The obtained polymers were applied as protective coatings for holographic films, and as materials for microlenses fabrication by inkjet printing technique.

Introduction High refractive index polymers and composites are widely used for obtaining optical micro- and nanostructures which find their application as protective coatings, microlenses, waveguides, etc. Nowadays the production of high refractive index polymers is possible by including heavy atoms such as sulfur, halogens, (except fluorine) in their structure. The best result of n (RI) was achieved in the order of 1.7-1.8 for a number of polymers based on poly (sulfo-2-(1,3,5-triisopropenylbenzene). Despite numerous papers describing investigation of RI for different classes of polymers, there is no data available for polymeric analogues of ionic liquids. It is well-known fact that such properties of PIL as thermostability, mechanical characteristics, ionic conductivity, etc. depend on the nature of the counterion. Generally known method of calculating the refractive index according to Askadskii A.A. is not suitable for ionic polymers because of absence of corresponding data. In this paper, the dependence of the RI on the nature of the counterion of PIL is studied for the first time and Askadskii method of calculating RI was adapted for PILs.

Main part. Two series of ionic polymers based on poly(dimethyldiallyl ammonium) cation and on ionic polyurethane with ammonium cation were synthesized. Three synthetic methods were applied for the ion exchange reactions depending on the nature of the desired anion. The exchange to hydrophobic anions was performed with an excess of alkali metal salts ($Li(CF_3SO_2)_2N$, $Li(FSO_2)_2N$) in an aqueous medium followed by precipitation of the respective PILs. The exchange to hydrophilic anions was carried out with the equimolar amount of silver salts ($AgCH_3COO$, $AgNO_3$, $AgCH_3C_4H_6SO_3$) accompanied by centrifugation and drying of resultant PIL or by dialysis (for Br, F and I ions). The structure of the synthesized polymers was confirmed by IR and NMR spectroscopy. For polymers that do not contain halogen, a Belstein probe was performed. Thermal degradation temperature of obtained polymers was investigated by thermal gravimetric analysis and was in the range from 315 to 416°C. The differential scanning calorimetry data revealed that some polymers are amorphous (with anions $(CF_3SO_2)_2N$, $ZnCl_3$) and some have crystalline nature (with anions Cl, F, Br, I, NO_3, CH_3COO, $(FSO_2)_2N$). The optical properties of ionic polymers were measured by ellipsometry and optical spectroscopy. Theoretical RI calculated by Askadskii method varies from 1.40 to 2.83, and according to experimental data from 1.44 to 1.73. Corresponding coefficients

for atoms in ionic form were calculated using an atomic additive empirical scheme based on experimental data. Density were calculated using Ab Initio calculations by optimizing the geometry of a number of cells (V ~ 1000 A3) with different conformations and mutual orientation of polymer chains. The obtained polymer with highest (RI) was successfully applied as a material for protective coatings. Also inks for inkjet printing with rheological parameters (viscosity 7.5 mPa·s, surface tension 41.6±0.2 mN/m) were made and microlenses (diameter 20 microns, height 0.96 microns) based on this polymer were printed.

Conclusions. Thus, novel ionic polymers with different types of counterion were synthesized and their optical properties were investigated. The dependence of the theoretically calculated refractive index of PILs on the experimental data is revealed. It was shown, that obtained polymers could be applied as protective coatings for interference images and rainbow holograms. The microlenses with a pitch of 70 microns, a diameter of 20 microns and a height of 0.96 microns were obtained by inkjet printing based on synthesized high refractive polymers.

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