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Surface properties of ionomers based on styrene-b-acrylic acid copolymers obtained by copolymerization in emulsion

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ABSTRACT

Surface properties of styrene-b-acrylic acid copolymers obtained in emulsion and suitable ionomers before and after UV-irradiation were studied by measurements of contact angles and FTIR-ATR spectroscopy.

The research focused on the influence of different content of carboxylic acid groups in copolymers, of various types and contents of alkali metal salts in ionomers and of cesium acrylate or methacrylate in ionomers on hydrophilicity of the surfaces of these samples and the course of photodegradation in them.

Hydrophilicity of initial copolymer surfaces was higher than this of polystyrene as a result of presence of carboxylic acid groups, which also made the surfaces of these copolymers more sensitive to UV-irradiation.

Hydrophilicity of the surfaces of ionomers containing cesium acrylates depended on the content of cesium salt in the samples. The course of ionomer photooxidation was also dependent on the content of this salt.

The surface of ionomer containing cesium methacrylate was more polar than this of ionomer containing cesium acrylate.

Styrene-based ionomers containing 3.7 mol% of various alkali metal acrylates had less polar surfaces than initial copolymer and they were also more resistant to UV-irradiation in comparison to the initial copolymer.

Copolymers obtained in emulsion and suitable ionomers had more polar surfaces and they were more sensitive to UV-light compared to copolymers obtained in bulk and their ionomers.

1. Introduction

Random ionomers are polymeric materials which consist of hydrophobic backbone chains along which there is a small number of ionic groups (up to 15 mol%) forming ion pairs. Interactions between these pairs cause association and formation of larger ionic aggregates. It is assumed that two types of aggregates are created in ionomers [1–3].

One type of the aggregates are multiplets, which are formed when the ion content in ionomers is low and whose size is about 0.6 nm. Multiplets are regions containing several ionic pairs and these regions are devoid of segments of polymeric chains. Formation of multiplets depends on size of ions as well as type of polymeric matrix. Thus small polar ions interact strongly and the multiplets are more compact than in the case of larger ions. In addition, electrostatic interactions between ion pairs have to overcome elastic forces of polymeric chains. When polymeric matrix is considered, it is vital that initial polymers have low dielectric constant and low T_g to facilitate multiplets formation. Sometimes steric hindrances, which may be branches of polymer chains, make the aggregation difficult. The multiplets are surrounded by polymeric chains, which are connected with ionic groups and the mobility of such surroundings is restricted. The limit of the regions of restricted mobility is not clear and it depends on the flexibility of the polymer chains. If polymer chains are flexible the multiplet surroundings are smaller. The presence of multiplets in ionomers causes their physical cross-linking.

With increasing ion content in ionomers larger aggregates are formed and they are called clusters. In this case there are more multiplets with the regions of restricted mobility that overlap due to their neighbourhood. Hence ion pairs and some polymeric chains are present in clusters which might be so large that they become phase-separated regions with their own T_g [1–3].

Applications of polymeric materials depend also on their surface structure. Physical and chemical features of outer layer of polymers differ from the features of the core of the materials. Several physical methods of surface modification, for instance:

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plasma, corona treatment, UV-, γ-irradiation, let us achieve a proper surface structure [4].

In order to determine the surface polarity, contact angles can be measured and next surface free energy can be calculated. Measurements of contact angles may help us to observe the changes in outer layer of polymers after modifications.

Surface properties of ionomers after plasma or plasma source ion implantation (PSII) treatment were studied by few scientist [5–9], who investigated hydrophobic recovery of styrene-based ionomers [5–8], methyl methacrylate-based and ethyl acrylate-based ionomers [9] after modification. Their studies indicated that the hydrophobic recovery of ionomers treated with plasma or PSII was slower than that of acid-form copolymers or non-ionic polymer due to the interactions between new oxidized groups and ionic groups which came out towards the ionomer surface.

Surface properties and changes after UV-irradiation of styrene-co-acrylic acid copolymers obtained in bulk and suitable ionomers were studied previously [10]. The measurements of contact angles and FTIR-ATR spectroscopy were applied to investigate the surface properties of copolymers containing 5.2 and 11.7 mol% of acrylic acid and suitable ionomers with Li^+, Na^+, K^+, Cs^+ cations. Influence of the content of cesium acrylates in ionomers on surface properties was examined as well.

The aim of this work was to investigate the alteration of the surface properties before and after UV-irradiation of styrene-b-acrylic acid copolymers obtained in emulsion and their ionomers (Fig. 1). It is considered that copolymers obtained in emulsion have longer sequences of acrylic acid due to the greater solubility of acrylic acid in water than in styrene and greater participation of these sequences formed in water phase in copolymers [11]. Copolymers obtained in emulsion had partially random and block structure, whereas copolymers obtained in bulk were random copolymers. It is worth comparing the surfaces of these two types of copolymers and ionomers, which because of different ways of formation, have different properties. It was indicated earlier that certain properties of ionomers based on copolymers obtained in bulk or in emulsion were different [12–16].

2. Experimental

The copolymers of styrene (S) and acrylic acid (AA) or methacrylic acid (MA) were obtained by copolymerization in emulsion [17]. To achieve suitable ionomers, solutions of 3–5% of the copolymers in benzene (for copolymers containing about or above 5 mol% of acid a mixture of benzene and methanol 9:1 v/v was used) were titrated under nitrogen by a standard solution of alkali metal hydroxide in methanol [18]. Some of these solutions were freeze-dried, and the others were used for obtaining films by evaporation of solvent at room temperature. The samples were dried to a constant weight at 323 K in vacuum.

The measurements of contact angles (Θ) of the films were carried out by the static sessile drop method using a DSA G10 goniometer of Krüss GmbH (Germany) at room temperature. The measurements were made with redistilled water (polar liquid) and diiodomethane (non-polar liquid). The liquid drop was placed onto the polymer surface with a microsyringe. The drop image was recorded by a video camera and digitalized. The profile of a single drop was numerically solved and fitted by means of mathematical functions. Each contact angle is the average value of 8 measurements and the deviation from the average is within ±2°.

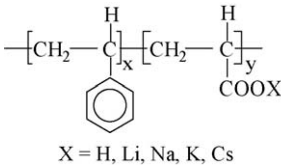

Fig. 1. Structure of S-b-AA (Li, Na, K, Cs).

Surface free energy (γ_s) as well as dispersive (γ_s^d) and polar (γ_s^p) components of the surface free energy were calculated on the basis of contact angle values by Owens–Wendt method [19], using an appropriate computer program.

The FTIR-ATR spectra of the films of all investigated polymers were recorded in the region 600–4000 cm^{-1} with a spectrophotometer FTIR Genesis II equipped with ATR (Pike Technologies, Inc.), containing ZnSe crystal, at room temperature.

The numbers in parentheses show the content of AA, MA or the appropriate salt comonomer in mol%. Letter "b" means that samples were obtained by emulsion copolymerization.

3. Results and discussion

Fig. 2 shows values of water contact angles measured on the surfaces of the films of polystyrene (PS) and styrene-b-acrylic acid copolymers (S-b-AA) with varied content of acrylic acid. The highest value of contact angle is characteristic of the unirradiated surface of polystyrene, which suggests that it is the most hydrophobic surface. The unirradiated surfaces of S-b-AA copolymers have lower values of contact angles than that of PS and the lowest value of contact angle is characteristic of the surface of S-b-AA copolymer with 3.7 mol% of acrylic acid. Thus introduction of carboxylic acid groups into PS chain makes the copolymer surfaces more polar.

In these studies FTIR-ATR spectra of the unirradiated copolymers obtained in emulsion were recorded to observe the differences in the spectra of these copolymers.

Absorption band corresponding to the carbonyl groups vibrations of unirradiated styrene-b-acrylic acid copolymers is shown in Fig. 3. Maximum of the band at about 1700 cm^{-1} is assigned to the vibrations of the dimers of carboxylic acids [20,21]. The highest value of absorbance is for the copolymer containing the highest content of acrylic acid. With decreasing content of carboxylic acid groups in copolymers the intensity of absorbance is decreasing. It means that the lower content of acrylic acid in copolymer the lower intensity of absorption band of dimerized carboxylic acid groups.

Maximum of the band at about 1740 cm^{-1} is assigned to the stretching vibrations of free carboxylic acid groups [20,21] and the intensity of this band is much lower than one at 1700 cm^{-1}. Thus the majority of the acrylic acid groups in outer layer of copolymers take part in the formation of hydrogen bonds.

As it was mentioned above the value of water contact angle is the lowest for copolymer with the lowest content of carboxylic acid (3.7 mol%). It suggests that water used as the test liquid

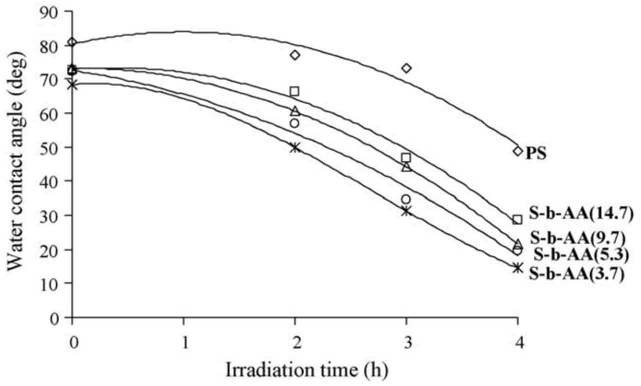

Fig. 2. Dependence of water contact angle on irradiation time of polystyrene and styrene-b-acrylic acid copolymers with various content (mol%) of acrylic acid.