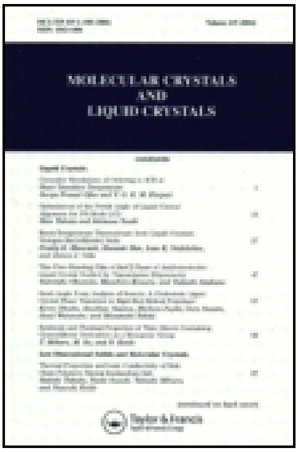

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Lithium Bonding in Acrylonitrile Copolymers and Nanocomposites with Ionic Conductivity

V. G. Syromyatnikov [a], A. T. Siniugina [a], I. A. Savchenko [a], L. P. Paskal [a], L. P. Linets [a] & A. Yu. Kolendo [a]

[a] Macromolecular Chemistry Department, Taras Shevchenko National University of Kyiv, Kyiv, Ukraine

Version of record first published: 03 Mar 2011

To cite this article: V. G. Syromyatnikov, A. T. Siniugina, I. A. Savchenko, L. P. Paskal, L. P. Linets & A. Yu. Kolendo (2011): Lithium Bonding in Acrylonitrile Copolymers and Nanocomposites with Ionic Conductivity, Molecular Crystals and Liquid Crystals, 536:1, 81/[313]-85/[317]

To link to this article: http://dx.doi.org/10.1080/15421406.2011.538350

Mol. Cryst. Liq. Cryst., Vol. 536: pp. 81/[313]–85/[317], 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.538350

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V. G. SYROMYATNIKOV, A. T. SINIUGINA,
I. A. SAVCHENKO, L. P. PASKAL, L. P. LINETS,
AND A. YU. KOLENDO

Macromolecular Chemistry Department, Taras Shevchenko National
University of Kyiv, Kyiv, Ukraine

Lithium is known to form complexes with organic compounds including polymers which have different kinds of bonding. Regular polymers as poly(ethylene oxide) can form crystalline complexes with ionic bonds with Li. In this work, statistical copolymers acrylonitrile – high methacrylates are synthesized, and their nanocomposites with a lithium salt are prepared. Their dielectric characteristics and ionic conductivity are studied. The results describe interactions between Li and copolymers which can be explained by the lithium bonding in systems.

Keywords Acrylonitrile copolymers; ionic conductivity; lithium complexes

Introduction

Lithium can form complexes with many organic compounds, e.g., monomers in the initiation of their polymerization. Its complexes with some polymers are widely applied as matrices for solid polymer electrolytes in lithium batteries [1,2]. First, only poly(ethylene oxide) was proposed [3] which can form typically ionic complexes with lithium salts. These complexes can be crystalline or amorphous depending on anions. The ionic conductance is provided by the amorphous phase in the poly(ethylene oxide) – salt composition due to the ion migration along a polymer chain via its segmental motion above the glass transition temperature. Therefore, it may serve as a reliable polymer matrix in lithium conducting polyelectrolytes only at temperatures above 80°C. A further approach to the improvement of service properties of polymer electrolytes at normal temperatures involves the application of another polymers or the bee of PEO with them [4].

The complexation between $LiClO_4$ and different polymers with a donating oxygen or nitrogen atom in the main chain, such as poly(propylene glycol), poly (iminoethylene) etc., was studied by means of conductometric titration, viscometry, NMR-spectroscopy. The occurrence of complexation was unequivocally proved [5]. We had studied copolymers of VBE-vinyl butyl ether which had oxygen atom in the

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Address correspondence to V. G. Syromyatnikov, Macromolecular Chemistry Department, Taras Shevchenko National University of Kyiv, 60, Volodymyrska Str., Kyiv 01033, Ukraine. E-mail: svg@univ.kiev.ua

back chain, with malic anhydride, butyl methacrylate, and methacrylic acid [6]. Ionic conductivity of their mixtures with $LiClO_4$ up to 10^{-6} Sm/cm was observed, but the complexes were formed only for monomer (VBE) mixtures with $LiClO_4$ studied with NMR-spectroscopy. The introduction of VBE copolymers in bends with PEO had improved their conductivity by more than one order of magnitude. Copolymers of methacrylic acid also had ionic conductivity, but their thermal characteristics had to be improved [7]. The next step in studying the lithium-polymer complexes was the macromolecular design inside acrylonitrile copolymers [8,9]. The last one has a nitrogen atom as a strong complex-forming center, and we predicted that its copolymers would be able to form complexes with lithium [10].

Lithium bonding is an interaction analogous to hydrogen bonding. Weak short-lived complexes are formed between Li ion and oxygen and/or nitrogen atoms of polymers [11,12]. They cannot be isolated and studied in ordinary way, but their presence can be found by studying the polymer properties, e.g., dielectric ones.

Experimental

Materials

All starting materials were commercially available (Aldrich). Monomers were distilled before copolymerization.

Polymer Synthesis

The copolymers of hexyl methacrylate (HMA), octyl methacrylate (OMA), and acrylonitrile (AN) were obtained by the radical copolymerization in the presence of 2,2′-azobis(isobutyronitrile) (AIBN) as a free radical initiator (1% wt.). The copolymerization was continued at 80°C for 5 h in a thermostat. The polymerization mixture was poured into methanol. The solid precipitates were filtered and then dried in vacuum at 60°C for 24 h. The copolymer compositions have been determined by the elemental analysis.

Preparation of Polymer Electrolytes

The unfilled copolymer films were formed by pressing the melt at 350–390 K at 15 MPa. The copolymer films filled with $LiClO_4$ salt were prepared by pouring the polymer solution containing $LiClO_4$ of different concentrations ($3 \sim 42$ mol.%) on Teflon or glass plates. These films were dried in vacuum up to a constant weight and then placed between two Teflon films to perform the dielectric measurements.

Measurements

These samples were used for studying the influence of functional groups and the component polarity on dielectric parameters and the conductivity, as well as on the complex-formation abilities, as estimated by the dielectric method. Dielectric measurements were carried out over the temperature range of 120–411 K and the frequency range of 0.7–15 kHz. The dielectric characteristics (dielectric constant ε', dielectric loss $tg\delta$, loss factor ε'', and effective conductivity σ) were measured using copolymer films with a thickness of 1.5–2.0 mm and a diameter of 25 mm.

Results and Discussion

Synthesis and Characterization

In order to clarify the influence of the monomer structure and its ratio in copolymers with AN on dielectric properties and the complexation with Li salts, some series of AN copolymers with monomers with butyl methacrylate (BMA), HMA, OMA and nonyl methacrylate (NMA) were synthesized with monomers ratios 1:1, 2:1, 3:1, and 4:1. Compositions of copolymers were proved by analytical methods. Dielectric measurements were carried out using, as samples, films made from these copolymers and their mixtures with $LiClO_4$.

Dielectric Properties

The dielectric measurement results for the acrylonitrile copolymer films of different chemical structures are shown in Figure 1. The curves tgδ *versus* T at a frequency of 1 kHz have one maximum which corresponds to the dipole-segmental relaxation. The location of $T(\mathrm{tg}\delta_{\max})$ depends on the chemical structure. Comparing the dielectrical parameters of copolymer films, it can be seen that an increase of the content of alkyl radicals in copolymers results in a decrease of the intermolecular interaction in macromolecules. The presence of a long alkyl group in the octyl methacrylate copolymer AN-OMA (1:1) molecule causes a shift of the α-relaxation maximum by 23 K (Fig. 1, curve 1) in comparison with the copolymer AN-BMA (1:1) (Fig. 1, curve 3). Such strong shift of $T(\mathrm{tg}\delta_{\max})$ to lower temperatures is due to the decreased intermolecular interaction in copolymer AN-OMA.

The temperature dependence of tgδ is shown in Figure 2 for copolymer films AN-OMA at various monomer ratios. The addition of the acrylonitrile polar component into copolymers chains results in a shift of $T(\mathrm{tg}\delta_{\max})$ to a higher

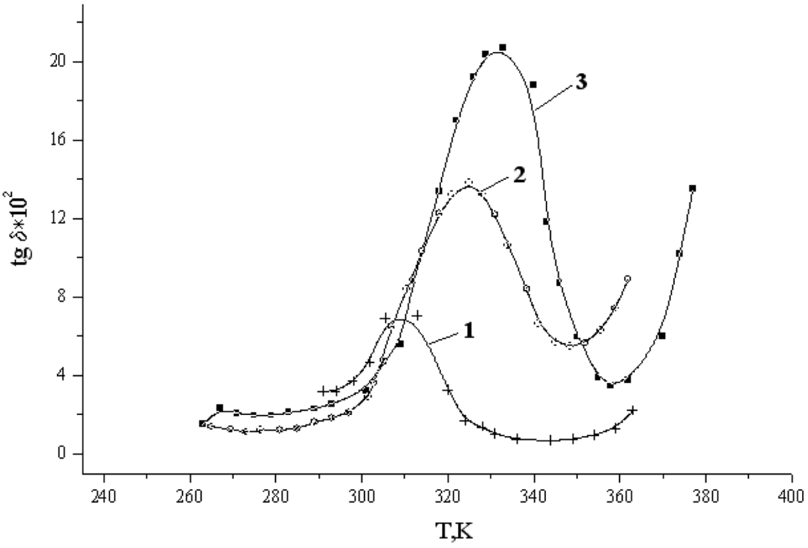

Figure 1. The temperature dependences of tgδ at 1 kHz for copolymers: 1 – AN-OMA (1:1), 2 – AN-HMA (1:1), 3 – AN-BMA (1:1).

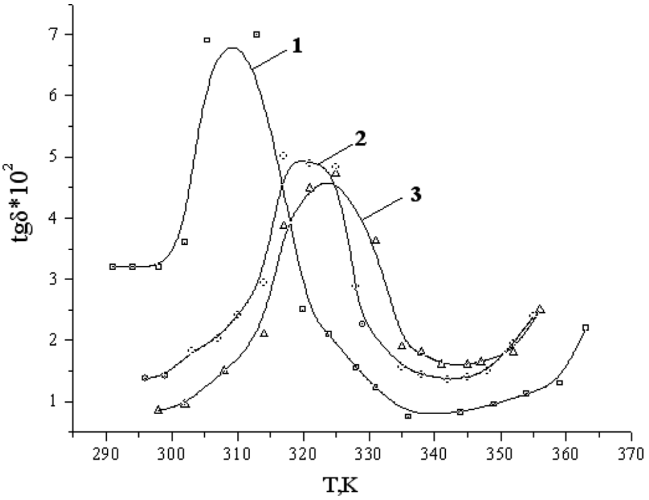

Figure 2. The temperature dependences of tgδ at 1 kHz for copolymers: 1 – AN-OMA (1:1), 2 – AN-OMA (2:1), 3 – AN-OMA (3:1).

temperature and a decrease of the absolute value of tg$\delta_{\max}$. The process of dipole-segmental relaxation was retired, and the intermolecular interaction and relaxation times of the α-process were decreased. It was caused by the influence of the polar nitrile group in copolymers.

Some copolymers have been chosen as matrices to form solid polymeric electrolytes. These copolymers were characterized by low glass temperatures. By adding the $LiClO_4$ salt to the methyl-ethyl ketone solution, its concentration was changed from 5% to 20% (weight). The temperature dependence of tgδ is shown in Figure 3 for copolymer films AN-OMA (2:1) with and without $LiClO_4$ salt.

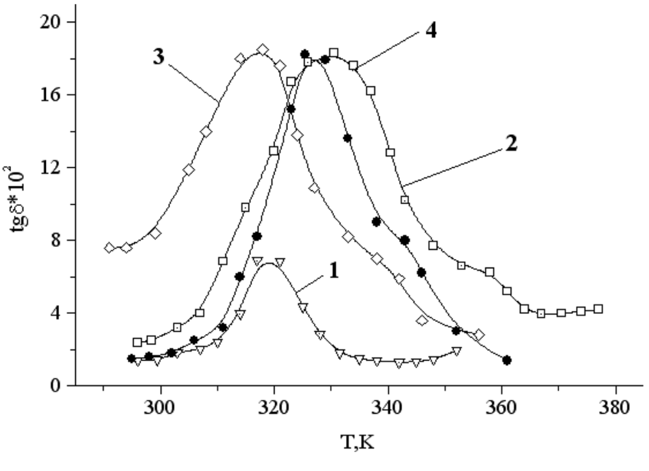

Figure 3. The temperature dependences of tgδ at 1 kHz for copolymers: 1 – AN-OMA (2:1), 2 – AN-OMA (2:1) + 5% $LiClO_4$, 3 – AN-OMA (2:1) + 10% $LiClO_4$, 4 – AN-OMA (2:1) + 20% $LiClO_4$.

The addition of $LiClO_4$ salt to the copolymer (Fig. 3, curves 2 and 3) results in the interaction of Li ions with oxygen and nitrogen atoms in monomer units with the formation of Li bonds. Each curve has a maximum and a shoulder, which correspond to two centers of complexation (O- and N-atoms).

The ionic conductivity values of solid polyelectrolyte films based on the investigated copolymers at 293 K are 10^{-6}–10^{-4} Sm/cm (10% $LiClO_4$), which evidences the ion-polymer complex formation in the system.

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