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Structure and Dielectric Behavior of *block* Copolymers Containing an LC Polyacrylate Block

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ABSTRACT: New block copolymers based on the ionogenic block of poly(*N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride) (PDADMACl) and liquid crystalline (LC) acrylate-based polymers are synthesized. The chain length of the acrylate-based block is controlled by the temperature and PDADMACl−acrylic monomer ratio. The chain length of the acrylate-based block controls the structure of the PDADMACl block whether crystalline or amorphous. Because of the "solid" state of the polyelectrolyte in domains both polymer and small ions are strongly fixed, and this provides the opportunity to reveal the polymer chain dynamics related with the LC acrylate-based polymer. The dynamics of the LC polymer in the block-copolymer is shown to be very similar to that in the homopolymer with no strong influence of polyelectrolyte blocks.

Introduction

In the last several years, block-copolymers containing liquid crystalline (LC) components became the subject of interest for scientists active in polymer synthesis, structure, and morphology.[1−5] The high activity in this field aims at exploration of new approaches for the preparation of block-copolymers based on blocks of different chemical structure as well as the development of new materials with the combined properties of LC and other functional polymers.

One of the methods tried for the preparation of block-copolymers is based on the use of poly(*N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride) (PDADMACl) as a polymer precursor (i.e., the first block). It is known that a degradative chain transfer of a monomer during the radical cyclopolymerization of *N*,*N*-diallyl-*N*,*N*-dimethylammonium chloride results in the formation of a terminal double bond.[6] The approach developed by Dragalova et al.[7] permits the activation of this double bond in the presence of the peroxide-containing radical initiator, and such a macromolecular compound with the immobilized peroxide may be used as the macroinitiator (or precursor).[8]

The object of this work was to apply this approach for the preparation of block-copolymers based on a water-soluble PDADMACl and LC polyacrylate−poly-[*p*-(ϵ-acryloyloxycaproyloxy)-*p*′-methoxyphenylbenzoate)] [PA(OCH3)] to find the main regularities for the synthesis of LC copolymers with the controlled hydrophilic−hydrophobic balance and to understand the mutual influence of the components on the phase behavior, structure, and morphology of block-copolymers as a whole as well as on the dynamic behavior of the LC component.

Experimental Section

The acrylic monomer, *p*-(ϵ-acryloyloxycaproyloxy)-*p*′-methoxyphenylbenzoate, as well as the corresponding homopolymer, was prepared as described in Mousa et al.[9] The main characteristics of the homopolymer as well as the related block-copolymers are given in Table 1. To prepare amphiphilic block copolymers in the alcohol solution, the macroinitiator based on PDADMACl (M_η = 6×10^4 g/mol) (0.1 mol/L) containing hydrogen peroxide (3 wt % of PDADMACl) was mixed with the mesogenic acrylic monomer.

The copolymerization in the methanol solution was carried out at 30 and 60 °C with PDADMACl/peroxide to acrylic monomer molar ratios of 1:5 and 10:5. The reaction mixture was degassed in a glass ampule (p = 0.04 Pa) by the freeze−thaw method. After reacting at 30 °C for several hours, the reaction mixture was washed with boiling methanol several times (to remove the residual PDADMACl and acrylic monomer). The acrylic homopolymer was removed by multiple extractions with benzene. If the polymerization reaction was carried out at 60 °C, the solvent was removed by rotory evaporation, and the residual substance was washed several times with both boiling benzene (to remove the acrylic homopolymer) and methanol (to remove the residual PDADMACl). After drying in a vacuum (p = 0.04 Pa), the structure of the resultant product was identified by ^{13}C NMR spectrum, whereas the copolymer composition was measured by ^{1}H NMR. The ^{13}C NMR and ^{1}H NMR spectra were recorded with an MSL-300 (Bruker) spectrometer.

The ^{13}C NMR spectra (Figure 1) show the set of different signals which are referenced to specific carbon atoms in the following structure:

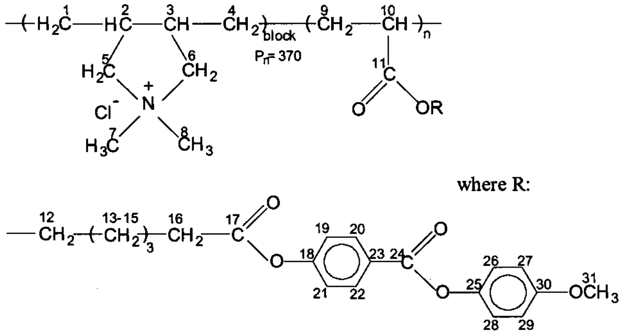

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Table 1. Solubility of Homopolymers and block Copolymers in Different Solvents

	polymerization conditions					
polymer	T, °C	PDADMACl/ monomer, mole	CH_3OH	benzene	$CHCl_3$	benzene/CH_3OH 5:3 (vol/vol)
PDADMACl	−	−	+	−	−	−
copolymer 1 (370:10)	60	10:3	−	−	−	+ (boil)
copolymer 2 (370:700)	30	1:3	−	gel	gel	−
PA(OCH_3)	−	−	−	+	+	−

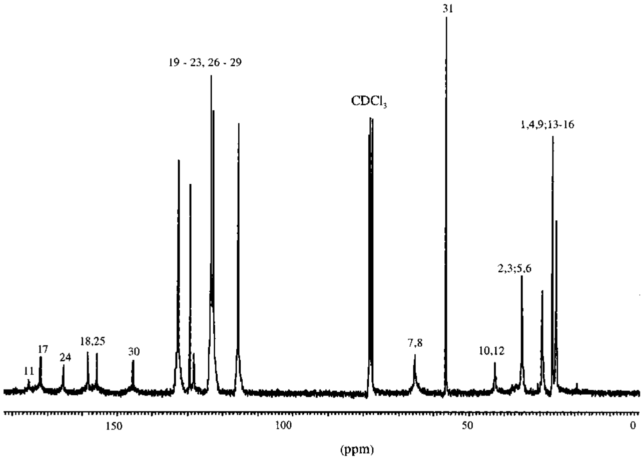


Figure 1. ^{13}C NMR spectrum of PDADMACl−PA(OCH_3) block copolymer 2.

The signal at 64.0 ppm is characteristic of carbon atoms of the methyl groups attached to a pyrrolidine ring (C-7 and -8), and the two set of signals in the range 30−40 ppm correspond to the C-atoms of the pyrrolidine ring (C-2, -3, -5, and -6).[10] At the same time, a set of signals are seen which correspond to carbon atoms in the LC polyacrylate side chain: C-11, -17, and -24 are related to the carboxylic group (164−175 ppm) and C-18, -25, and -30 and C-19−23, and C-26−29 to the benzene rings (at 144−159 ppm and 112−134 ppm respectively).

^{1}H NMR spectra were used for the analysis of the copolymer composition; the ratio of the integral signal intensities of methylene groups at the nitrogen atom (4.0 ppm) and the total integral intensity of H-atoms in benzene rings (8.6−10.5 ppm) were calculated.

X-ray diffraction measurements were carried out using DRON-3.0 (Cu Kα radiation, Ni-filtered, and in the transmission mode).

The thermal behavior of the polymers was studied by DSC (Mettler TA-4000) with a heating/cooling rate of 10 K/min.

The thermomechanical curves for the polymers were obtained with a handmade instrument VIP-70M at the infinitely low load (dilatometry regime).

The copolymer film with the thickness of 0.2 mm for X-ray measurements was prepared under pressure at 2×10^9 Pa and 100 °C for 1 h, and then it was cooled to room temperature. To orient the copolymer film, the sample was stretched at 40 °C up to $\lambda = 1.8$ and then cooled to room temperature while secured with clamps.

Dielectric measurements were carried out in a glass cell coated with gold electrodes. As a distance holder, 0.1 mm thick glass plates situated outside of the gold electrodes were used. The calibration of the cell was done with cyclohexane. Capacities C and resistance R were measured by a Solarton−Schlumberger impedance analyzer SI1260 in combination with a Chelsea dielectric interface at different frequencies f. The temperature was controlled by an Eurotherm regulator. The measurements were carried out on polydomain samples because the application of the external magnetic field of 0.7 T as well as electrical bias of 35 V did not result in the formation of oriented samples. The data were fitted at different temperatures to the extended Cole−Cole equation[11]

$$\epsilon^* = \epsilon_2 + \frac{\epsilon_0 - \epsilon_1}{1 + (j\omega\tau_1)^{1-\alpha_1}} + \frac{\epsilon_1 - \epsilon_2}{1 + (j\omega\tau_2)^{1-\alpha_2}} + \frac{A}{f} \quad (1)$$

containing two dielectric absorption ranges and an empirical conductivity contribution. From the given complex dielectric constant ϵ^*, only the imaginary part with the dielectric increments $\Delta_{i+1} = \epsilon_i - \epsilon_{i+1}$, relaxation times τ_{i+1}, and distribution parameters α_{i+1} was taken into account.

The block copolymer was prepared as a film because it was not possible to bring it into the real fluid state, and this film was introduced between two gold electrodes with no spacer inside. Furthermore, the electrodes were pressed together with an external clamp to keep the sample from changing its shape. In this case, capacities C' and losses $C'' = (2\pi fR)^{-1}$ (R = measured resistance) were used for calculations. The given quantities are connected by the same calibration constants $\epsilon'' = KC''$ and $\epsilon' = KC' + L$ (L = additional small capacity from the cables). Thus, eq 1 can also be used for fitting the C'' and C' data.

Results and Discussion

PDADMACl is a long-chain polymer that may be considered a macromonomer that contains a double bond at the end of the macromolecule chain. As shown in Dragalova et al.,[7] this double bond may be activated and start the radical polymerization of vinyl monomers at an elevated temperature. As shown in Talroze et al.,[8] the high yield of the copolymer product when the acrylic monomer, cetylacrylate, is polymerized in the presence of the PDADMACl macroinitiator may be achieved if the copolymerization reaction proceeds at 30 °C in the methanol solution. That is why the copolymerization of PDADMACl and the mesogen-containing acrylic monomer was carried out at the same conditions. In this case, careful treatment with the selective solvents (which take homopolymers out of the resultant product) results in the isolation of the residual products which have solubility essentially different from that of homopolymers (Table 1).

At the same time, one can see (Table 1) that similarly to what is shown in Talroze et al.[8] the solubility of the polymerization products depends on the polymerization reaction conditions. With increases in the temperature (60 °C) and macroinitiator−acrylic monomer ratio, the resultant product becomes soluble in the boiling benzene/methanol (5:3 vol/vol) mixture. In contrast to that, the polymerization product prepared at 30 °C is not soluble

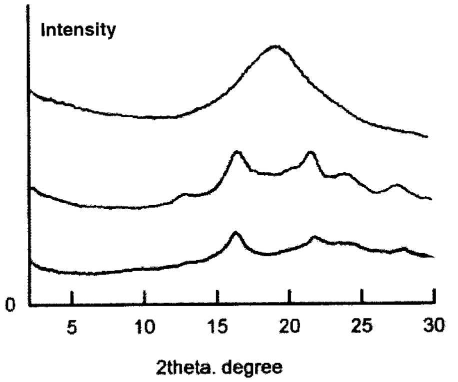
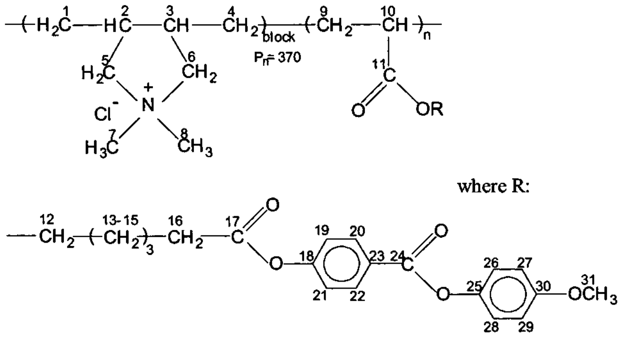


Figure 2. X-ray of DADMACl (1), block copolymer 1 (2), and block copolymer 2 (3).

in the above mixture and shows a limited swelling in benzene and $CHCl_3$. The ^{13}C NMR spectra (Figure 1) of the resultant products described above reveal the presence of both PDADMACl and polyacrylate units within the polymer product. These data, combined with variations in the solubility of resultant products, show that this approach permits the synthesis of copolymers based on the hydrophilic block of the PDADMACl macroinitiator and the LC polymer. One may assume that the change in the solubility of different copolymers results from the change in the length of the hydrophobic block at a constant chain length of the initial ionogenic macroinitiator ($P_\eta = 370$) used: The general formulas for the copolymer PDADMACl−$PA(OCH_3)$ synthesized are



As it comes from the calculations based on ^1H NMR data, the copolymer synthesized at 60 °C contains a short sequence of the acrylic units ($n = 11$) (sample 1). The second sample prepared at the lower temperature (30 °C) and much lower PDADMACl/H_2O_2 to acrylic monomer ratio (1:5) consists of the long chain block of PDADMACl and the long block of the acrylic polymer ($n = 700$) (sample 2).

The presence of the semicrystalline structure of a solid PDADMACl is easily seen from the X-ray diffractogram of sample 1 (Figure 2, curve 1). Wide-angle X-ray reflections (Figure 2, curve 2) coincide with those known for the crystalline PDADMACl (Figure 2, curve1). The crystalline structure of this copolymer (sample 1) does not change with heating (the PDADMACl melting point is above the temperature of its decomposition, which starts at 150 °C), and as shown by the thermomechanical curve (Figure 3, curve1), there is no deformation registered in the sample under the constant load within a wide temperature range. Taking into account the copolymer 1 composition, which corresponds to the volume fraction of the PDADMACl block equal to 0.9, and the data mentioned above one may guess that solid PDADMACl plays the role of matrix which provides the mechanical and structural properties of the copolymer as a whole, whereas the LC nematic polymer is organized in the form of small domains.

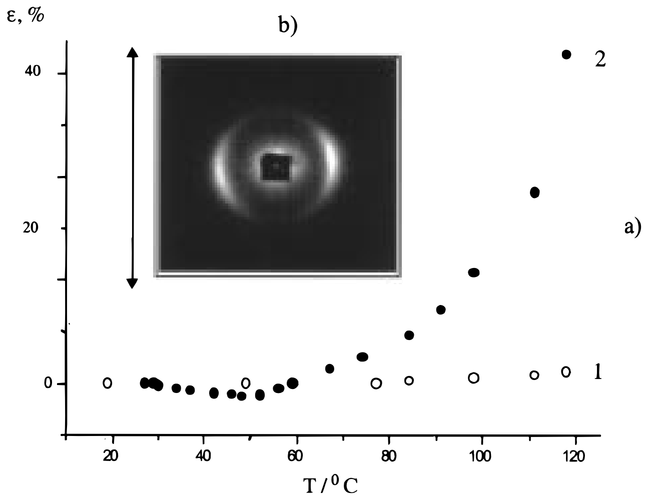


Figure 3. (a) Thermomechanical curves of PDADMACl−PA(OCH_3) block copolymer 1 (1) and block copolymer 2 (2). (b) X-ray textured pattern of block copolymer 2. The stretching axis is indicated with an arrow.

Table 2. Transition Temperatures and Transition Enthalpy for Homopolymer and Block Copolymers of Different Compositions

polymer	T_g (°C)	T_{NI}, (°C)	ΔH_{NI} (J/g)
$PA(OCH_3)$ ($P_n = 190$)	15	110	1.0
copolymer 2 (370:700)	27	131	0.7

Just the opposite situation is observed for copolymer 2 ($n = 700$). In this case, X-ray diffraction (Figure 2, curve 3) does not register the presence of the PDADMACl crystals (although the presence of its block is fairly proved by NMR), whereas the glass− and nematic−isotropic transitions (Table 2) known for the LC polymer are clearly seen in DSC curves. The latter is also shown by the presence of the optically anisotropic texture, which exists at room temperature and above and appears and disappears at about 130 °C (T_c).

The absence of any sign of the crystalline structure of PDADMACl in copolymer 2 agrees well with prior observations that the crystallization of the PDADMACl block is essentially restricted under the influence of the long crystallizable block of the acrylic polymer-like polycetylacrylate.[8] In our case, we deal only with the nematic, ordered acrylic system, but even here, the lengthening of the acrylic block makes impossible the crystallization of the hydrophilic block. In contrast to that for copolymer 1, the thermomechanical curve for copolymer 2 (Figure 3, curve 2) shows a slight deformation of the material right above T_g. The strong deformation of the sample resulting from the copolymer flow is developed with the rise of the temperature while approaching the T_{n-i} phase-transition temperature. Taking into account the volume content of the LC polymer block in copolymer 2, which is equal 0.8, we may anticipate that in this copolymer the phase inversion takes place as it was shown for different LC block copolymers in Fisher et al.[12,13] In this case, the matrix is formed by the LC block, which provides the mechanical response of the material as a whole. That is why the stretching of the film results in the partial orienta-

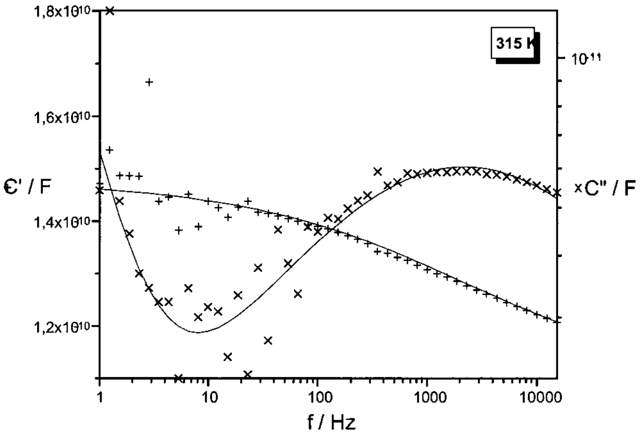


Figure 4. Real and imaginary part of the capacitance. (The fit parameters are $C(0) = 147$ pF, $C(1) = 110$ pF, $\tau = 75$ ms, $\alpha = 0.61$, $A = 5.76 \times 10^{-12}$ Hz).

tion of the sample, as is seen from the localization of the amorphous halo at wide angles at the equator of the textured X-ray pattern (Figure 3). One may suppose that the orientation proceeds in LC domains with the LC director aligned parallel to the stretching axis. This serves also as a sign for the diblock structure of the copolymer under study.

Thus, the structure and thermal properties of copolymer 2 prove the presence of the LC block in the copolymer. The question arises to what extent the dynamics of the LC block within the microphase is similar to that for the corresponding LC homopolymer though it is fixed “from one end” by molecules of the “solid” polyelectrolyte.

The dielectric measurements should give an idea about the dynamic behavior of LC blocks in the copolymer. On the other hand, one could expect that the presence of the polyelectrolyte block within the copolymer may cause a high conductivity which would not allow the measurement of the dielectric absorption. However, as is shown here, the conductivity of copolymer 2 is low enough to permit dielectric measurements. At the same time, this also indicates a solidlike behavior for the domains containing ions of PDADMACl.

In Figure 4, the losses C'' and the capacitances C' at different frequencies are given. We could detect only one dielectrically active process that may be used to characterize the dynamic behavior of the copolymer as a whole. The experimental points were fitted to the complex eq 1 using only one absorption range and the conductivity part. The respective fitting curves are also shown in Figure 4. Because of the small losses, the data are uncertain at low frequencies. The obtained increment is about 30% of the entire dielectric function, and the distribution parameter is equal to 0.65–0.7. In contrast to that of the block copolymer, the 3-D plot of the dielectric loss in a homopolymer (Figure 5) shows two different relaxation processes. The distribution parameter α_2 for the faster process varies between 0.65 and 0.7 and coincides with that for the copolymer, whereas α_1 at lower frequencies is calculated to be between 0.2 and 0.26. The related increments are 2.5 for the high- and 0.6 for the low-frequency processes. Because of the fast (high-frequency) process, the dielectric constant decreases about 30%. The relaxation times are presented in Figure 6.

The faster process detected in the homopolymer may be discussed as α-relaxation connected with the motion of the main chain. A fit to the Vogel–Fulcher–Tamman,

$$\ln(f_R) = \ln(f_0) - A/(T - T_0) \qquad (2)$$

results in a Vogel temperature[14] T_0 of 267 K for the homopolymer, which should be 30–50 K below the T_g. This is in good agreement with the T_g of PA(OCH_3) measured by DSC. The slope of the $\tau(T)$ curve for the copolymer is also practically parallel to that of α-relaxation in the homopolymer. Furthermore, the relative dielectric increments and the Cole–Cole distribution parameters are the same. These data suggests that the absorption detected in copolymer 2 is also the α-relaxation related to the acrylate backbone in the LC block. The segment mobility of the acrylate polymer chain in the block-copolymer seems to not be strongly influenced by the second solid block of PDADMACl, and this also proves the microphase-separated structure of the copolymer.

The slower dielectrically active process in the homopolymer characterized by the low dielectric increment is related to the reorientation of the mesogenic side groups[15] and is often called the δ-mechanism. The absence of this process in copolymer 2 may be a surprise, but as is shown, the δ-relaxation cannot be detected as well in our homopolymer after heating the sample up to the isotropic state and cooling it down to the LC

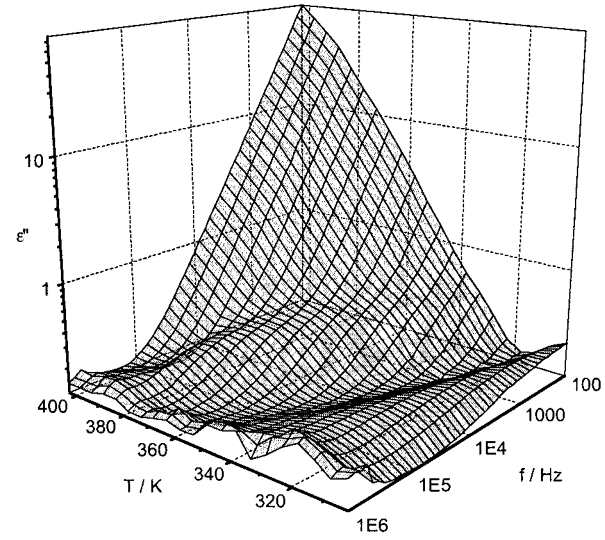


Figure 5. 3D plot of the dielectric loss of PA(OCH_3).

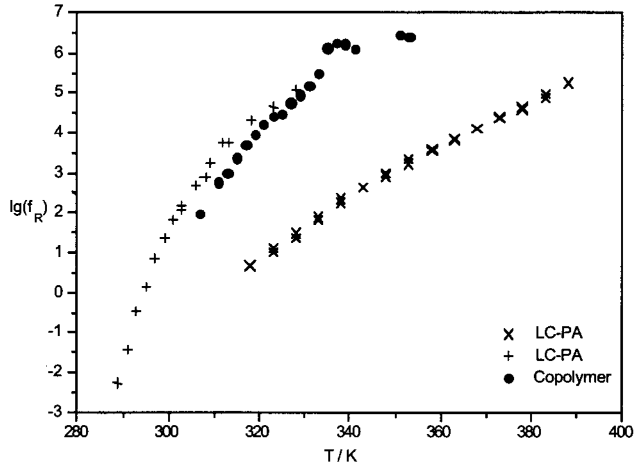


Figure 6. Relaxation frequencies of PA(OCH_3) and PDADMACl–PA(OCH_3) versus the absolute temperature.

phase. The main reasons for this should be the spontaneous, nearly planar orientation of the side mesogenic groups and the low absorption intensity. In this case, any small longitudinal dipole moment of the side group cannot be detected. Taking into account that the copolymer sample used for dielectric measurements was prepared under pressure to keep a flat filmlike shape between the two electrodes, one may assume that at such conditions the planar orientation of mesogenes is achieved within the LC domains, which does not permit the observation of the δ-relaxation in the copolymer. Contrary to this, the α-process is related to the statistically distributed main chain and should be dielectrically active in any direction.

Thus, one may conclude that the synthetic approach used here permits the creation of new copolymers based on the ionogenic polymer PDADMACl. The control over the chain length of the acrylate-based block permits the regulation of the structure of the PDADMACl block whether crystalline or amorphous. Because of the solid state of the polyelectrolyte in domains both poly- and small ions are strongly fixed, and this provides the opportunity to reveal the polymer chain dynamics related to the LC acrylate-based polymer. The dynamics of the LC polymer in the block-copolymer is shown to be very similar to that in the homopolymer with no strong influence of the other blocks, which also proves the domain structure of the copolymer as a whole.

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