

Effect of polymer structure on the molecular dynamics and thermal behavior of poly(allyl acetoacetate) and copolymers



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ABSTRACT

In this paper, dielectric and calorimetric studies of the small-molecule glass former allyl acetoacetate monomers as well as its newly synthesized homopolymer and copolymers with different styrene composition were performed in both the liquid and glassy states. The molecular dynamics studies by the broadband dielectric spectroscopy and the stochastic temperature modulated differential scanning calorimetry enabled us to explore relaxation processes of examined materials in the wide frequency range. We found that the copolymers reveal two co-existing glass transitions characterized by the glass transition temperatures, which are very close to those of the corresponding homopolymers. These results suggest that the copolymers exhibited some sequences of acetoacetate units with a microphase-separated morphology in agreement with the value of reactivity ratio previously determined. We investigated effects of copolymerization compositions on the glass transition temperature, the isobaric fragility index, the dielectric and calorimetric intensity, and the dynamic heterogeneity on the glass transitions of the materials.

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1. Introduction

Synthetic polymers containing tautomeric functional groups have emerged as important materials due to their potential applications. The presence of tautomeric units on the main polymer chain was used to immobilize different ion. In particular, allyl acetate is a very interesting organic compound to complex many transition metal ions. The interest of this group as ligand has increased recently due to unique magnetic or catalytic properties of the complex particles [1]. Papaphilippou et al., studied a series of copolymers including 2-(acetoacetoxy)ethyl methacrylate metal-chelating monomer, in which β -ketoester functionalities act as effective stabilizers for iron oxide nanoparticles in aqueous solutions [2]. Subsequently, Pd nanoparticles encapsulated in AEMA-containing diblock copolymer micelles were synthesized and investigated towards nonlinear optical (NLO) properties [3]. The most studied tautomeric monomers are β -dicarbonyl derivatives, mainly due to the ease of synthesis and prior knowledge of structurally related compounds of low molecular weight [4,5]. Among β -

dicarbonyl monomers, allyl acetate has been extensively studied by Bartlett and Altschul in a radical polymerization process [6]. In this reaction, a competition between the fundamental reactions of addition to the double bond (polymerization) and hydrogen abstraction (chain transfer) can be observed [7]. Recently, we have synthesized and characterized two kinds of tautomeric acetoacetate copolymers with different compositions, structure and properties [8].

Besides the chemical characterization of the newly synthesized copolymers it is very important to investigate their thermal behavior and molecular dynamics under different conditions. Determining the molecular mobility of copolymers enables us to gain a better insight into properties of copolymers, in particular dynamics of the glass transition, which are strongly dependent on the composition, architecture, and morphology of the copolymers. Such investigations can consequently lead to an improvement of the polymeric materials. A very useful method for establishing molecular mobility of polymers is the broadband dielectric spectroscopy (BDS), which enables measurements of relaxation times over a wide frequency range up to 12 decades at different temperatures. The BDS study can be combined with the temperature modulated differential scanning calorimetry (TMDSC) measurements, which usually cover only a narrow frequency range near the

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glass transition, but can facilitate the identification of the origin of relaxation processes observed in the dielectric and mechanical spectra [9]. Homopolymers and more complex systems like copolymers usually exhibit several relaxation processes of different nature in the dielectric relaxation spectra. In polymers, the main relaxation process (α -relaxation) associated with the glass transition temperature is related to segmental dynamics of the chain. Besides the linear-chain polymers, dielectric analysis has been applied to numerous macromolecular systems with complex molecular architectures, namely, comblike and branched structures, stars, cycles, copolymers (alternate, statistical, di or multiblock copolymers), physically or chemically bonded polymer networks, hyperbranched polymers, and dendrimers. The molecular dynamics of such systems involves a series of relaxation processes that goes from very local motions (generally due to branching chains or side-chains) to segmental mobility exhibiting cooperativity (α relaxation), or even large-scale relaxation processes (Rouse dynamics or reptation) [10,11]. For instance, some block copolymers have complex phase diagram that may show microphase separation [12,13] and they can reveal more than one segmental relaxation associated with the glass transition of each block [14–21]. The temperature behavior of structural relaxation times of each block is usually similar to that of the corresponding homopolymer [22]. However, the shape of the structural relaxation is much broader in copolymers than that in homopolymers, which is often related to an increase in the dynamic heterogeneity or cooperativity of segmental motions in copolymers [15,22]. These investigations have been considerably enriched by high pressure measurements [23], enabling for instance an additional verification of ideas that originally assumed ambient pressure conditions. Besides segmental dynamics the secondary relaxations can be also observed in dielectric spectra of polymers. The secondary processes usually reflect some fluctuations of parts of the polymer mainchain, conformational changes in cyclic side groups, or hindered rotations of side groups or parts of them [10,11,24–27]. This type of local dynamics remains active even when the polymer is in the glassy state, that is, when the large lengthscale backbone motions are frozen.

In this paper, we report results of a comparative analysis of allyl acetoacetate (AAA) monomer, its homopolymer and two copolymers with styrene (St-co-AAA) of different mole fraction of monomer AAA, i.e. $F_{AAA} = 0.45$ (St-co-AAA1) and $F_{AAA} = 0.17$ (St-co-AAA2). We focus on molecular dynamics studies of the materials in the wide temperature range in both the liquid and glassy states by using the broadband dielectric spectroscopy and stochastic temperature modulated differential scanning calorimetry. We investigate the effect of the polymer structure on the molecular dynamics and thermal behavior properties of PAAA and poly(St-co-AAA).

2. Experimental section

2.1. Materials

Allyl acetoacetate monomer (AAA, 98%, Aldrich) was used as received. The initiator, 2,2'-azobis(isobutyronitrile) (AIBN, 98%, Merck) was purified by recrystallization from methanol before use. Methanol (99.9%, Aldrich), chloroform (RPE, Carlo Erba), acetonitrile (HPLC, Sintorgan), tetrahydrofuran (RPE, Carlo Erba), sodium bicarbonate (99.5%, Fluka), and anhydrous sodium sulfate (99%, Anedra) were used as received without further purification. Styrene (>99%, Aldrich) was freed from inhibitor by washing with aqueous NaOH solution (10 wt%) and then with water until neutrality, dried over anhydrous sodium sulfate, and distilled under reduced pressure before use.

Polymerization: PAAA homopolymer and two poly(St-co-AAA) copolymers were synthesized by mass radical polymerization with azobisisobutyronitrile as a radical initiator, as described by Giussi et al. in a previous paper [8]. Briefly, different amounts of both comonomers (total weight 10 ml) were introduced into a reaction tube with a pre-weighed amount of initiator (35 mM). The mixtures were degassed by three freeze–pump–thaw cycles in a vacuum line system, then sealed and immersed into a thermostat at 333 K at different times in the absence of light. After the reaction, polymers were precipitated with methanol and purified by three steps of dissolutions in chloroform and precipitation in methanol, centrifuged and dried under vacuum. This procedure was repeated until only the peak of the polymer was seen by size-exclusion chromatography (SEC). The chemical structure of the obtained copolymer is shown in Fig. 1.

Two copolymers poly(St-co-AAA)1 and poly(St-co-AAA)2 with different monomer composition were synthesized, starting at the same initial monomer feed, $F_{AAA} = 0.80$, at 4 and 16 h, respectively.

Characterization: The ^1H NMR and ^{13}C NMR spectra of the samples were recorded with a Bruker Spectrometer, 300 MHz. Chloroform- d_1 was used as a solvent for the polymer. The sample concentrations were 0.4 and 6.0 wt% for monomer and polymer respectively. The measurements were carried out at 313 K.

The copolymers obtained were identified by NMR. ^1H NMR (300 MHz, chloroform- d_1 , ppm) δ : 1.49 ($>\text{CH}-\text{CH}_2-$ St and AAA); 1.95 ($>\text{CH}-\text{CH}_2-$ St and AAA); 2.13 ($\text{CH}_3-\text{C}(\text{O})-$ keto and $\text{CH}_3-\text{C}(\text{OH})=\text{enol}$ AAA); 3.53 ($-\text{C}(\text{O})-\text{CH}_2-\text{C}(\text{O})-$ AAA); 4.13 ($-\text{CH}_2-\text{O}-\text{C}(\text{O})-$ AAA); 5.06 ($-\text{C}(\text{OH})=\text{CH}-\text{C}=\text{O}-$ enol AAA); 6.5–7.5 (ArH St). ^{13}C NMR (300 MHz, Chloroform- d_1 , ppm) δ : 21.15 ($-\text{CH}_3$ enol); 30.23 ($-\text{CH}_3$ keto); 32.50 ($>\text{CH}-\text{CH}_2-$ AAA); 40.55 ($>\text{CH}-\text{CH}_2-$ AAA); 42.78 ($>\text{CH}-\text{CH}_2-$ St); 44.06 ($>\text{CH}-\text{CH}_2-$ St); 49.92 ($-\text{C}(\text{O})-\text{CH}_2-\text{C}(\text{O})-$ keto); 68.02 ($>\text{CH}-\text{CH}_2-\text{O}-\text{C}(\text{O})-$); 89.75 ($-\text{C}(\text{O})-\text{CH}=\text{COH}$); 125.66 (ortho- C Ar); 127.72 (meta- C Ar); 128.02 (para- C Ar); 145.29 (ipso- C Ar); 166.88 ($>\text{C}=\text{O}$ ester); 175.31 ($\text{HO}-\text{C}=\text{O}$ enol); 200.01 ($>\text{C}=\text{O}$ keto).

The copolymer compositions were estimated from the integral ratio of selected peaks of ^1H NMR, using the following formula [8]: $F_{AAA} = 5I_{\text{CH}_2}(\text{h}) / (5I_{\text{CH}_2}(\text{h}) + 2I_{\text{Ar}})$, where I_{CH_2} and I_{Ar} are the intensity of the signals of allyl ($\delta = 4.13$ ppm) and aromatic hydrogen ($\delta = 6.5\text{--}7.5$ ppm), respectively.

The average molecular weight and the molecular weight distribution were determined by SEC in an LKB-2249 instrument at 298 K. A series of four μ -styragel columns (10^5 , 10^4 , 10^3 , 100 Å pore size) were used with chloroform as an eluent. The polymer concentration was 4–5 mg/mL, and the flow rate was 0.5 mL/min. The polymer was analyzed using double detection as previously reported [28]. Mass chromatograms of the polymers were detected by a Shimadzu (SPD-10A) UV/VIS detector at 254 nm (for the phenyl group), while the carbonyl group was detected by infrared (IR) absorption at 5.75 μm with a Miram 1A spectrophotometer detector. Polystyrene standard supplied by Polymer Laboratories and Polysciences were used for calibration.

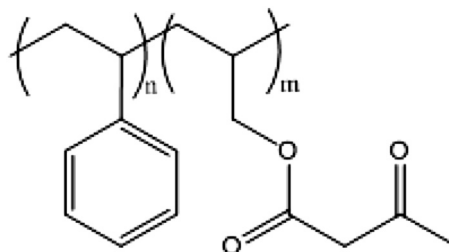


Fig. 1. Chemical structure of synthesized copolymers poly(St-co-AAA).

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