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Tautomeric acetoacetate monomers as building units of functional copolymers

Juan M. Giussi [a,b,c], Iwona Blaszczyk-Lezak [c], Belen Sanz [c], Patricia E. Allegretti [b], Carmen Mijangos [c,*], M. Susana Cortizo [a,b,*]

[a] *Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CONICET CCT-La Plata, Argentina*
[b] *Laboratorio de Estudio de Compuestos Orgánicos (LADECOR), Facultad de Ciencias Exactas, UNLP (1900), 47 y 115, La Plata, Argentina*
[c] *Instituto de Ciencia y Tecnología de Polímeros, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

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ABSTRACT

Although synthetic polymers from tautomeric functional monomers have emerged as a new kind of materials due to potential applications their interest needs still to be revealed. In this work we have synthesized two series of tautomeric acetoacetate copolymers, with different composition, microstructure and properties. We have selected allyl acetoacetate (AAA) and 2-(acetoacetoxy)ethyl methacrylate (AEMA) monomers to copolymerize with styrene (St). The bulk copolymerization initiated with azobisisobutyronitrile was carried out at 60 °C for different monomer feed compositions and times. The products were characterized by ^{1}H NMR, HSQC NMR and size exclusion chromatography. The calculated monomer reactivity ratio obtained for poly(St-co-AAA) and for poly(St-co-AEMA), show noteworthy differences in the copolymerization behavior; r_1r_2 take values near 1 and zero for poly(St-co-AAA) and poly(St-co-AEMA), respectively. The glass transition temperature (T_g) values for copolymers were determined by differential scanning calorimetry. Two T_g temperatures were found for poly(St-co-AAA) which were close to the T_g values of corresponding homopolymers. On the other hand, only one T_g values characterized the St-co-AEMA copolymers system. Thermal stability has been studied by thermo gravimetric analysis (TGA). The copolymers St-co-AAA and St-co-AEMA exhibited higher thermal stability than homopolymer AAA and AEMA, respectively. Due to the functional group present in both monomers, they exhibit tautomeric equilibrium; an interesting NMR study in solution allowed us to demonstrate that the displacement of equilibrium depends on composition, microstructure and solvents. In view of future applications as nanomatrices for tissue engineering, these tautomeric copolymers (St-co-AAA), were nanostructured in AAO nanocavities and its morphological and surface characteristics analyzed by SEM.

1. Introduction

Synthetic polymers containing tautomeric functional groups have emerged as important materials due to their potential applications, mainly as bidentate ligand for metal-chelating. The most studied were β-dicarbonyl derivatives, mainly due to the ease of synthesis and prior knowledge of structurally related compounds of low molecular weight [1,2]. The existence of tautomeric units on the main polymer chain is the relevant structural characteristic of this materials, which determine their applications, such as, to immobilize different ions in the synthesis of polymeric material with a high Pd(II) content. The via ring opening metathesis polymerization of

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[*] Corresponding authors. Address: Instituto de Investigaciones Fisicoquímicas Teóricas y Aplicadas (INIFTA), CONICET CCT-La Plata, Argentina (M.S. Cortizo).

E-mail addresses: cmijangos@ictp.csic.es (C. Mijangos), gcortizo@inifta.unlp.edu.ar (M.S. Cortizo).

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Pd(II)-containing monomer β-diketone was developed for catalytic application [3]. Masuda et al. studied the kinetics of the polymerization of MMA initiated by the binary system of poly(ethyl 3-oxo-4-pentenoate and cobalt(II) nitrate, utilizing the capacity of the allylacetoacetate as bidentate ligand based on its tautomeric forms [4]. This material was tested for separation and determination of ruthenium in environmental samples. Krasia-Christoforou 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 [5]. Subsequently, Pd nanoparticles encapsulated in AEMA-containing diblock copolymer micelles were synthesized and investigated towards nonlinear optical properties [6]. In a very interesting review, Tillet et al. showed that acetoacetyl groups can be used as key functional groups that enable the crosslinking of polymers by reaction with different reagents, allowing broadening its range of applications [7].

In order to understand the relationship between the tautomeric structure and its polymerizability, a series of unsaturated β-diketones and β-ketoesters have been investigated as monomer in radical polymerization [8]. These studies not only showed that the monomer reactivity is a function of the experimental reaction conditions, such as temperature, solvent and comonomer composition, but also demonstrated, that the displacement of tautomeric equilibrium in the monomers significantly influence the polymerization reactivity.

In a previous work, we studied the polymerization of an unsaturated β-ketonitrile monomer under different solvent conditions as well as the tautomeric equilibrium of the copolymers obtained [9]. This study allowed us to conclude that, for this functional monomer, the increase of the solvent polarity increased the enol content, both in the monomer and in the copolymer and that solution behavior is a consequence of different intra or intermolecular interactions, depending on the solvent polarity. Very recently we reported the mechanical and thermal properties of these copolymers as well as no evidences of cytotoxicity effects. These results allowed us to demonstrate that these materials exhibit high potential for the fabrication of scaffolds for tissue engineering. Subsequently, these copolymers were successfully nanoconfined in anodized alumina template (AAO) in order to obtain nanofibers for building extracellular matrices [10].

Thus, the tautomeric groups appear as building units of functional copolymers where the macromolecular structure could be changed as a function of the environment around of this material. This ability is relevant in biomedical applications due to the cell adhesion and proliferation depends of the hydrophobic/hydrophilic balance, as was previously demonstrate [11].

In order to enlarge this kind of tautomerics polymer materials and to deepen understanding the effect of the tautomerism on the structure and properties of polymers with functional tautomeric groups we designed two new copolymers based on tautomerizable monomers, which included β-ketoesters moiety: allyl acetoacetate (AAA) and 2-(acetoacetoxy)ethyl methacrylate (AEMA). In this work we report the copolymer synthesis as a function of reaction conditions and we analyze the effect of the composition on the thermal properties and transition of the obtained polymeric materials, as well as on the tautomeric effect and reactivity ratio. Finally, some of them were nanostructured in alumina templates in order to study the feasibility to produce large aspect ratio nanofibers.

2. Experimental

2.1. Materials

Styrene monomer (>99%, Aldrich) was freed from inhibitor by washing with NaOH aqueous solution (10 wt%) and then with water until neutrality, dried over anhydrous sodium sulfate, and distilled under reduced pressure before use. Allyl acetoacetate monomer (AAA, 98%, Aldrich) and 2-(acetoacetoxy)ethyl methacrylate monomer (AEMA, 95%, Aldrich) were 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%, Anhedra) were used as received without further purification.

2.2. Polymerization

Two families of tautomeric copolymers were synthetized, starting from allyl acetoacetate (AAA) or 2-(acetoacetoxy)ethyl methacrylate (AEMA) and styrene named poly(St-co-AAA) and poly(St-co-AEMA), respectively.

The copolymers were synthesized by mass radical polymerization with azobisisobutyronitrile as a radical initiator, as previously reported [9]. 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 60 °C at different times in the absence of light. After the reaction, the polymers were precipitated with methanol and purified by three steps of dissolution in chloroform and precipitation in methanol, centrifuged and dried under vacuum. The purity of copolymers was confirmed by size-exclusion chromatography (SEC).

2.3. Polymer characterization

2.3.1. Chemical characterization

The ^{1}H NMR spectra of the monomers were recorded with a Bruker Spectrometer, 300 MHz. Chloroform-d$_1$, carbon tetrachloride and dimethyl sulfoxide-d$_6$, were used as solvent in order to study the solvent effect in the tautomeric equilibrium of the monomers (the concentration was 0.4 wt%). In the case of polymers, ^{1}H NMR and ^{13}C NMR spectra were recorded, only Chloroform-d$_1$ was used as solvent because the samples are not soluble in carbon