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Metal catalyzed free radical copolymerization of allyl chloroacetate and N-propyl maleimide: a mass spectrometry study

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Summary

The copolymerization of allyl chloroacetate (ACAc) and N-propyl maleimide (PMI), catalyzed by Cu(I)Br or ferric(III) acetylacetonate (Fe(acac)$_3$) at 110 °C, respectively, was studied through electron-impact mass spectrometry. Both Cu(I)Br and Fe(acac)$_3$ catalyzed the copolymerization by an atom transfer process. However, the copolymerization of ACAc and PMI was not in an alternative way, because propyl maleimide has high tendency to form homogeneous polymeric segments under the conditions of this work.

Introduction

The design and development of controlled radical polymerization techniques is one of the most important contributions of the last decade to the field of chain-growth polymerization. The three most efficient controlled/”living” radical polymerization methods are nitroxyl radical-mediated polymerization [1], reversible-addition-fragmentation transfer polymerization [2], and atom transfer radical polymerization (ATRP) [3].

The ATRP mechanism is a radical polymerization where propagating radicals are generated and terminated by reversible ligand transfer to metal complexes, for example, using copper(I) [4-5], ruthenium(II) [6-7], Ni(II) [8-9], and Fe(II) [10-11] to catalyze the atom transform equilibrium. Cu(I) is often used to activate reversibly the dormant polymer chains by a halogen atom transfer reaction [12-14]. In Cu(I) based systems, 2, 2’-bipyridyl (bpy) is needed to solubilize and to selectively stabilize the Cu(I).

Facile synthesis of functional halogen initiators for ATRP has been shown to be extremely useful in designing molecules of complex topology, for example, hyperbranched polymers. In the course of developing methods for the synthesis of hyperbranched polymers, we have come to the conclusion that electron donor-acceptor monomers are very versatile building blocks for the direct synthesis of such polymers [15]. In this work, we study the copolymerization of allyl chloroacetate (ACAc) and propyl maleimide (PMI) catalyzed by Cu(I)Br/bpy and ferric (III) acetylacetonate ($Fe(acac)_3$) in an effort to explore new ATRP systems for producing hyperbranched polymers. In this system, a radical is expected to be formed by a chlorine atom transfer reaction, followed by initiation of copolymerization of PMI and ACAc. Maleimides [16] are often reported to form alternating copolymers with allyl compounds via a possible charge transfer complex [17]. A few studies of the reactions between maleimide and allyl compounds initiated by conventional free radical initiators indicated that the alternating mechanism in the copolymerization was prevailing, however, maleimide homopolymerization could be detected at temperature above 200 ^{o}C [18]. It is interesting to study the alternative tendency of the copolymerization between ACAc and PMI under controlled reaction conditions.

Experimental

Materials and methods

All solvents used were analytical grade. The following chemicals are used as received: ferric (III) acetylacetonate ($Fe(acac)_3$) (99%, Aldrich), maleic anhydride (99%, Acros), propylamine (analytical, Fluka), chloroacetic acid (99%, Aldrich), Cu(I)Br (98%, Fluka), 2,2’-bipylidyl (analytical, Aldrich), allyl alcohol (99%, Aldrich).

N-n-propyl maleimide (PMI) was synthesized according to reference [19]. Allyl chloroacetate (ACAc) was synthesized by an esterization reaction of chloroacetic acid and allyl alcohol. Their structures and purity were verified by ^{1}H/^{13}C NMR and gas chromatography - mass spectrometry (GC-MS).

Polymer synthesis and characterization

A mixture of ACAc (1g, 7.4 mmol), PMI (1g, 7.2 mmol), and catalysts was agitated under Argon atmosphere at 110 ^{o}C for 11 hours. Unreacted monomers were removed by vacuum at 100 ^{o}C. The catalyst systems used in this work are: (1) Cu(I)Br system; CuBr (0.10g, 0.7 mmol), bpy (0.22g, 1.4 mmol). (2) $Fe(acac)_3$ system; $Fe(acac)_3$ (0.20g, 0.5 mmol). (3) $Fe(acac)_3$/Fe system; $Fe(acac)_3$ (0.20g, 0.5 mmol), iron powder (0.20g).

Electron impact mass spectrometry (EI-MS) measurements were performed on a Fison’s ZabSpec mass spectrometer with an m/z range of 1500. Samples are introduced by direct insertion method with maximum probe temperature of 600 ^{o}C. Ionization was accomplished by electron impact at 70 eV.

The molecular weights of the polymers were measured by a size-exclusion chromatograph (SEC) using a 2142 differential refractometer manufactured by Pharmacia, and a linear column (AN gel linear) from American Polymer Standards Corporation. Tetrahydrofuran eluent was pumped at 0.5 ml/min at 40 ^{o}C. Polystyrene standards (Perkin-Elmer) were used for calibration.

Results and Discussion

Possibly because of the strong termination tendency of allyl groups, these systems are inactive to radical polymerization in the three initiating systems. The molecular weights in these systems developed very slowly, and were determined by GPC to be 750, 600 and 400 for CuBr, $Fe(acac)_3$, and $Fe(acac)_3$/Fe systems respectively. Perhaps high contents of initiators are needed in these systems to obtain high molecular weight polymers. However, we are interested in information on copolymerization of ACAc – PMI, and these initiator systems revealed by mass spectrometry study of these small polymers. Because only oligomers with a few repeating units were obtained during these copolymerizations, it is possible to obtain sufficient sample vapor pressure by direct-inlet probe for electron-impact ionization mass spectrometry analysis.

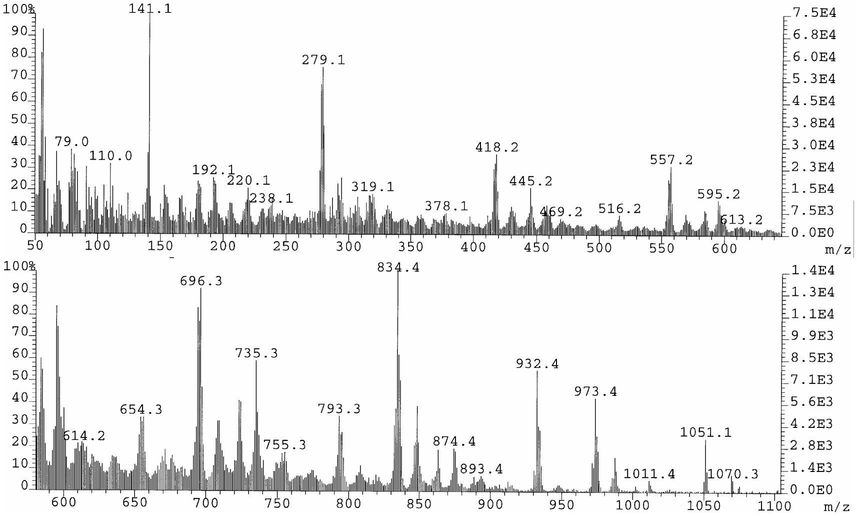
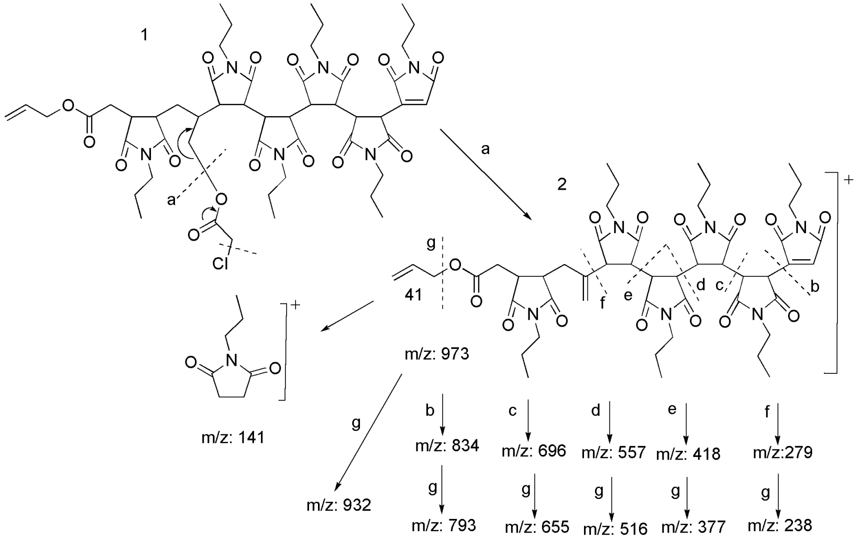


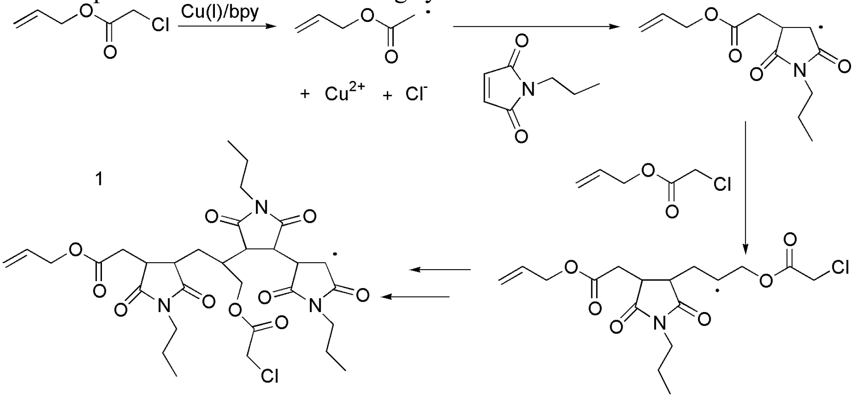
Figure 1. EI-MS of poly(ACAc-co-PMI) obtained from CuBr/bpy system



Scheme 1. Mass fragmentation pathways of poly(ACAc-co-PMI)

1. Cu(I)Br system

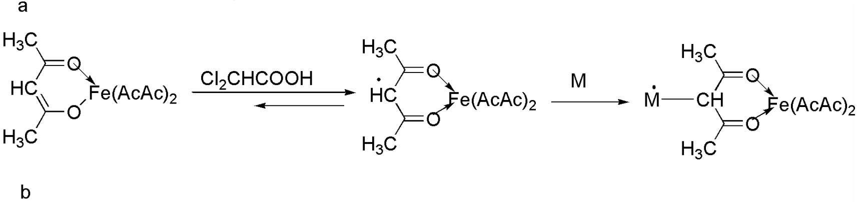
The EI-MS spectrum of the obtained polymer was depicted in Figure 1, that clearly showed repeating units with each mass of 139, i.e. polymeric PMI units, according to the peaks at masses 279, 418, 557, 696, 834, 973. The plausible mass fragmentation pathways were schematically illustrated in Scheme 1. These pathways can rationalize most significant peaks in the EI-MS spectrum of Figure 1. Allyl group can form a conjugated structure with the adjacent oxygen. Hence allyl ester groups are more stable than chloroacetate groups with respect to fragmentation, and parent ions are formed by cleavage of chloroacetate groups. Obviously, copolymerization of ACAc and PMI is not carried out in an alternative way. PMI has high tendency to form homopolymeric segments in the conditions of this work, at 110 °C. The possible reaction process in the CuBr initiating system was illustrated in Scheme 2.



Scheme 2. Polymerization of PMI and ACAc initiated by CuBr/bpy

2. $Fe(acac)_3$ and $Fe(acac)_3/Fe$ systems

$Fe(acac)_3$ has long been used to initiate grafting of vinyl monomers onto wool or cellulose in the presence of chloro-compounds, e.g. dichloroacetic acid, 1,2-dichloroethane, by a free-radical mechanism [20]. Two plausible mechanisms have been put forward, as illustrated as routes **a** and **b** in Scheme 3. Route **a** was suggested by Yoshikuni, et al [20a], where a diacetylmethyl radical was thought to be formed and initiate the radical polymerization. Whereas **b** could be tracked back to the work of Bamford, et al when dealing with grafting acrylate monomers onto wool fiber initiated by Cu(II)-acetylacetonate in the presence of trichloroacetic acid [21], where an atom transfer reaction happened through red-ox processes, followed by the formation of initiating radicals.

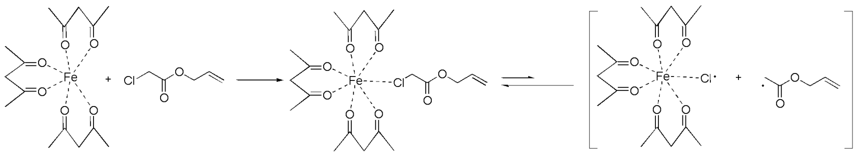


b

$$Fe(III) + R\cdot \longrightarrow Fe(II) + R$$

$$Fe(II) + Cl_2CHCOOH \longrightarrow \cdot CClHCH2OOH + Cl^-$$

Scheme 3. Two mechanisms of $Fe(acac)_3$ catalyst suggested in references



Scheme 4. Fe(acac)$_3$ catalyzed atom transfer process to form a radical

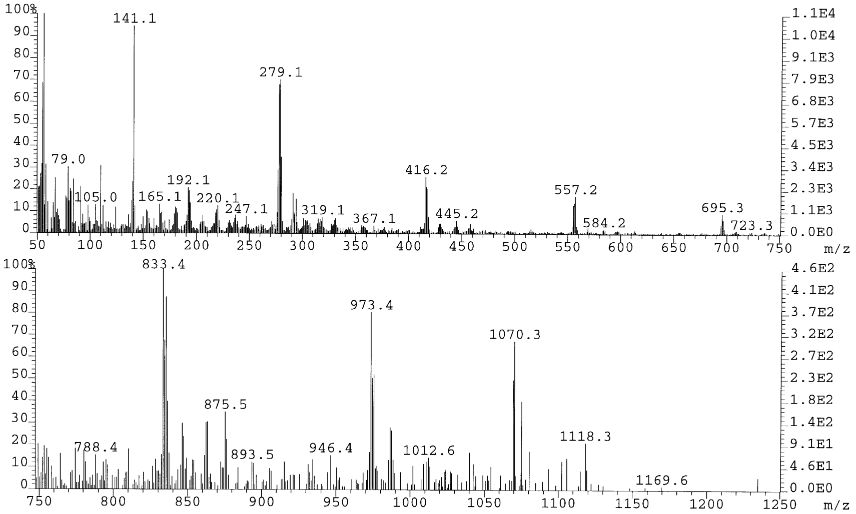


Figure 2. EI-MS of poly(ACAc-co-PMI) obtained in Fe(acac)$_3$ initiating system

The polymer obtained in Fe(acac)$_3$ initiating system of this work showed the same fragmentation pattern as that obtained in CuBr system (Figure 2). Thus, the obtained polymer started from the allyloxy-acetyl radicals, formed by a reaction like chlorine atom transfer reaction. However, route **b** in Scheme 3 cannot wholly interpret initiating process of Fe(acac)$_3$ under the conditions described in this work. According to route **b** in Scheme 3, addition of iron powder could improve the initiating activity, because higher concentration of Fe(II) could be expected from the addition of iron powder to Fe(acac)$_3$. On the contrary, the reaction was significantly suppressed when iron powder was added to the Fe(acac)$_3$ system, i.e. initiating system (3) in this work. Both yield and molecular weight were decreased in system (3). Thus, the atom transfer process to form allyloxy-acetyl radicals by Fe(acac)$_3$ is possibly by way of coordination of chlorine to Fe(III). The possible mechanism was depicted in Scheme 4. Allyl chloroacetate possibly formed a ligand to Fe(III), followed by an even cleavage of Cl-C bond to form a radical under elevated temperature. Fe(acac)$_3$ can be possibly used as a catalyst for controlled free radical polymerization.

Figure 3 is the EI-MS of the polymer obtained from Fe(acac)$_3$/Fe system. Both molecular weight and yield of the polymer are significantly decreased. The peak at mass of 279 in Figure 3 indicates the initiating allyloxy-acetyl radical.

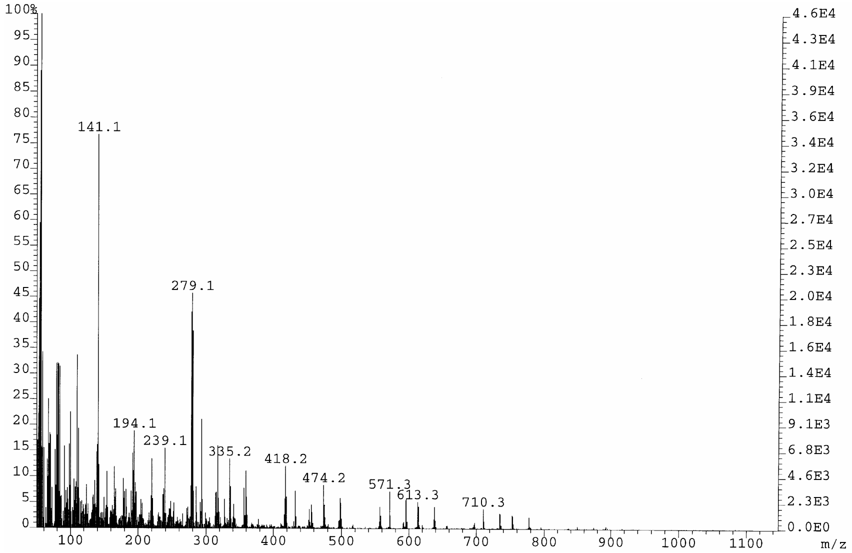


Figure 3. EI-MS of the polymer obtained in $Fe(acac)_3/Fe$ system

Conclusion

The MS studies showed that the copolymerization of PMI and ACAc is initiated by allyloxy acetyl radicals. It can be concluded that both Cu(I)Br and $Fe(acac)_3$ catalyzed the copolymerization by an atom transfer process on ACAc. The $Fe(acac)_3$ initiating system effects possibly through coordination properties of Fe(III). In addition, the copolymerization of PMI and ACAc was not in an alternative way, because PMI has high tendency to form homogeneous polymer.

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