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COPOLYMERIZATION OF METHYL METHACRYLATE WITH STYRENE INITIATED BY THIOL

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ABSTRACT

Tert.– dodencanethiol can initiate the copolymerization of methyl methacrylate (MMA) and styrene (St) near room temperature. Experimental results indicate that tert. – dodencanethiol (RSH) influences the initial rate of copolymerization (R_p) only insignificantly, when its concentration ranges from 4.3×10^{-4} to 2.7×10^{-2} mol / l; R_p increases as [MMA] in monomer composition is increased; the activation energy of the copolymerization at 30℃ ~ 45℃ is determined to be 56.4kJ / mol; the fact that the molecular weight of the copolymer decreases as [RSH] is increased indicated that thiol acts in the reaction not only as an initiator but also as a chaintransfer agent.

INTRODUCTION

It has been reported that thiol can initiate the radical copolymerization of maleic anhydride / styrene(1). So thiol is considered to be only able to initiate the copolymerization of those monomers which can form charge transfer complex, such as acrylonitrile / styrene(2), N–phenyl maleic imide / styrene(3)etc. Such a reaction mechanism is suggested that the first free radicals are generated by the proton transfer from thiol to the charge transfer complexes(4).

Thiol can also initiate the radical copolymerization of (MMA) and (St) effectively. We have studied the influences of [RSH], temperature and monomer composition on the copolymerization rate. The relation between the molecular weight of copolymers and [RSH], between the composition of copolymers and of monomers are discussed. The monomer reactivity ratios are calculated.

EXPERIMENTAL

Method of Polymerization

The polymerization is carried out in an exact calibrated dilatometer. All reagents have undergone strict purifying and drying pretreatment. The solvent methyl ethyl ketone is analytically pure and the initiator tert. – dodecanethiol also AR from the market. The dilatometer with reactants in it is placed in a super constant – temperature bath which has been regulated. After the reaction has begun, the volume change of the reaction liquid in the dilatometer is registered regularly. The weight conversion degree of the reaction is controlled under 10%. The polymerizate is separated out by anhydrous ethanol as precipitating agent, then washed and dried. The relation between the initial rate of polymerization R_p (mol • l^{-1} • s^{-1}) and volume change is shown by the following equation:

$$R_p = \triangle V \cdot 1000 / [\overline{M}_0 \cdot V_o(1/d_o - 1/d_p)]$$

where $\triangle$V is the decrease in volume per unit time (ml • s^{-1}), $\overline{M}_o$ the average molecular weight of the two monomers, $V_0$the volume of liquid before polymerization (ml), $d_0$the average density of the two monomers and $d_p$the density of the resulting polymerizate (g • ml^{-1}).

Analysis and Characterization

The density is measured with specific gravity bottle in constant temperature bath. The composition of copolymers is determined by means of elementary analysis and their molecular weight with the instrument Waters 100.

RESULTS AND DISCUSSION

The Thermodynamics of St / MMA Copolymerization

Without RSH in the system, no polymerization reaction is observed within five hrs. If tert. – dodecanethiol is added (concentration 10^{-4}~ 10^{-2}mol • l^{-1}), polymerization occurs already within 30 min. in dilatometer. The dependence of initial rate of polymerization R_p on [RSH] is studied for the case of equal mole

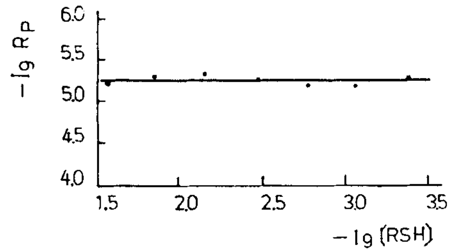

Fig.1 Relation between $R_p$and RSH
[MMA] = [St] = 4.50 mol • l^{-1}, temperature:40℃, solvent: methyl ethyl ketone

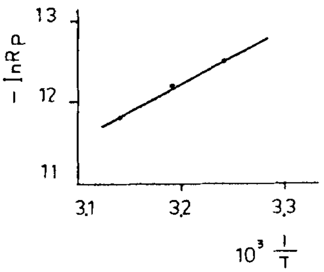

Fig.2 $R_p \sim T(K)$ relationship
[RSH] = 3.42×10^{-3} mol • l^{-1}, [MMA] = [St] = 4.50 mol • l^{-1}, solvent: methyl ethyl ketone

fractions in the monomer feed. The result (Fig.1) shows that R_p changes only slightly although [RSH] varies over a range of 3200 times, i.e., $R_p \propto [RSH]^0$. Study on the copolymerization of styrene and maleic anhydride has given a similar result⁽¹⁾.

In the case of equal [RSH], we have studied the relation between $R_p$and temperature T in the range of 35℃ ~ 45℃ (Fig.2). From the slope of $R_p \sim 1/T$ straight line, the activation energy $E_a$of the reaction is calculated to be about 56.4 KJ / mol.

Varying the mole fractions in monomer feed, we have also investigated the influence of [MMA] in monomers upon R_p. It is found that $R_p$is proportional to mole fraction of MMA f_{MMA}, as shown in Fig.3. Experimental results indicate that RSH shows no initiation function when $f_{MMA} = 0$ but when $f_{MMA} = 1$ it does. The mechanism of chain initiation could be considered to be so: at the be-

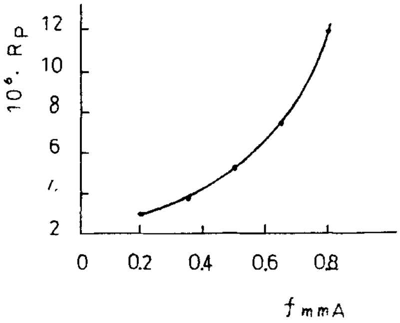

Fig.3 Relation between $R_p$and f_{MMA}

[MMA]+[St] = 9.0 mol • l^{-1}, [RSH] = 3.42×10^{-3}mol • l^{-1}, temperature: 40℃, solvent: methyl ethyl ketone

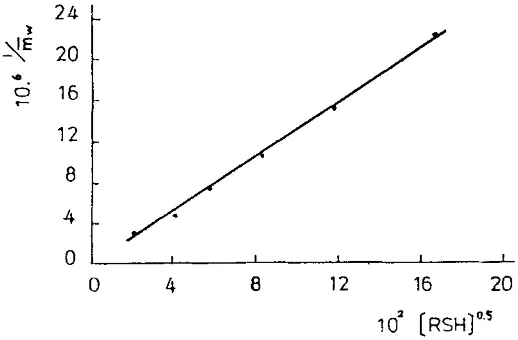

Fig.4 Relation between $\overline{M_w}$ and [RSH]

[MMA] = [St] = 4.50 mol • l^{-1}, temperature: 40℃, solvent: methyl ethyl ketone

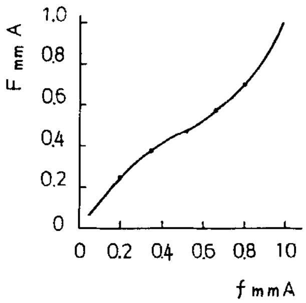

Fig.5 Relation between monomer composition and copolymer composition

gining the thiol initiates MMA, then the chain radicals react with St to form copolymer chain.

Effect of [RSH] on the Molecular Weight of Copolymers

The molecular weight of the resulting copolymers is measured for different RSH. $1/\overline{M}_w$ is found to be proportional to a power of 0.5 of [RSH], as shown in Fig.4. From the results it could be concluded that thiol acts only as initiator at lower concentration, but at higher concentration it acts as both initiator and molecular weight regulator, considering the insignificant effect of [RSH] upon R_p. The molecular weight is depressed as a result of radical chain transfer reaction. It is consistent with the conventional function of thiol as molecular weight regulator in polymerization.

The Composition of Copolymers

Keeping the total monomer concentration ($[M_0]$ $=9.0\text{mol} \cdot l^{-1}$) and [RSH] constant, varying the monomer fractions, elementary analysis is applied to the resulting products and the mole fractions of two monomers in copolymers are determined. The relation between copolymer and monomer composition is shown in Fig.5.

It could be found that the mole fraction of MMA in polymer increases evidently as [MMA] in monomer feed is increased. From the $f_{MMA} \sim F_{MMA}$ relationship, the monomer reactivity ratios are calculated: $r_{St}=0.65 \pm 0.02$; $r_{MMA}=0.46 \pm 0.02$, which are very close to the reported values of the reactivity ratios of St und MMA for radical copolymerization: $r_{St}=0.52 \pm 0.026$, $r_{MMA}=0.46 \pm 0.026$(5).

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