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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

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To cite this Article Wang, Gongshan , Xia, Ping , Yan, Deyue and Wang, Kangcheng(1991) 'Copolymerization of Acrylonitrile with Methyl Methacrylate Initiated by Thiol', Journal of Macromolecular Science, Part A, 28: 11, 257 – 263

To link to this Article: DOI: 10.1080/00222339108054408

URL: <http://dx.doi.org/10.1080/00222339108054408>

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COPOLYMERIZATION OF ACRYLONITRILE WITH METHYL METHACRYLATE INITIATED BY THIOL

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ABSTRACT

In this work, the authors found that thiol is capable of initiating the copolymerization of methyl methacrylate (MMA) and acrylonitrile (AN) at room temperature. The copolymerization kinetics, copolymer composition and molecular weight of the copolymer were studied. The apparent activation energy of the overall copolymerization was measured to be 143kJ/mol.

INTRODUCTION

Due to the relatively weak bond, S-H, thiol can easily be attacked by a radical, and therefore is often used as a molecular weight regulator in free radical polymerization. On the other hand, thiol as a component of redox system can promote the emulsion copolymerization of styrene with butadiene^{1,2}. Recently, it was reported that thiol alone can initiate the copolymerization of CTC (Charge Transfer Complex) comonomers such as styrene/acrylonitrile³ and styrene/N-phenylmaleimide⁴. However, thiol fails to initiate the homopolymerization of either monomer of the CTC comonomers. This work found that methyl methacrylate (MMA)/acrylonitrile (AN) can also be initiated to copolymerize by thiol,

even though MMA / AN is not a pair of CTC comonomer. The kinetic studies of the copolymerization of MMA / AN initiated by thiol is given below.

EXPERIMENT SECTION

Materials: MMA, polymerization grade, dried with CaH_2 , was distilled at reduced pressure immediately before use. AN, polymerization grade, was distilled at reduced pressure as well before use. 2-methyl-2-undecanethiol was a commercial product of Fluka AG Company. Solvents were dried and distilled before use.

Copolymerization: Copolymerization kinetic studies were carried out in dilatometers. Monomer conversion was controlled less than 5%. The monomer conversion and the initial copolymerization rate are given by the following expressions respectively (in $\text{mol} \cdot \text{l}^{-1} \cdot \text{S}^{-1}$):

$$C = \Delta V / [W_0(1/d_0 - 1/d_p)]$$

and

$$R_p = \Delta V \cdot 1000 / [\bar{M}_0 \cdot V_0(1/d_0 - 1/d_p)]$$

where C denotes monomer conversion (in weight fraction), \bar{M}_0 is average-molecular weight of the monomer units in copolymer, W_0 represents the total weight of comonomers, $1/d_p$ is the specific volume of the copolymer, $1/d_0$ is the specific volume of the monomer mixture, the composition of which is the same as that of the respective copolymer, ΔV (in $\text{ml} \cdot \text{S}^{-1}$) is the contraction of the reactant volume, V_0 is the initial reactant volume.

Analysis and characterization: The density was measured by a pycnometer; the copolymer composition was obtained from nitrogen elemental analysis; molecular weights were determined by GPC.

RESULTS AND DISCUSSION

Kinetic studies on the copolymerization of MMA with AN

The kinetic studies were performed at 40°C using methyl ethyl ketone (MEK) as solvent. No polymerization was observed in the reaction system of MMA / AN without RSH within 4h. When a trace amount of 2-methyl-2-undecanethiol was added, the copolymerization proceeded

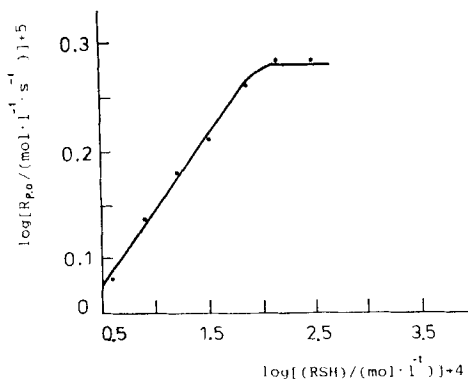


Figure 1, Relationship between initial copolymerization rate, R_{po} and thiol concentration, $[RSH]$; $[MMA] = [AN] = 4.51 \text{ mol/l}$, solvent: methyl ethyl ketone, temp.: 40°C .

smoothly. The influence of the concentration of RSH on the initial polymerization rate, R_{po} , is shown in Figure 1. When $[RSH]$ increases from $4.3 \cdot 10^{-4} \text{ mol/l}$ to $1.37 \cdot 10^{-2} \text{ mol/l}$, R_{po} also increases proportionally; if $[RSH]$ is more than $1.37 \cdot 10^{-2} \text{ mol/l}$, R_{po} keeps almost constant. These data indicate that thiol plays a double role, i.e., initiator and chain transfer agent. At large $[RSH]$, a violent chain transfer from propagating radicals to thiol results in that R_{po} remains unchanged. In addition, phenol can inhibit the copolymerization, and therefore the free radical feature of the reaction is confirmed.

The relationship between R_{po} and reaction temperature T is given in Figure 2. The apparent activation energy of the overall copolymerization is calculated to be 143 kJ/mol , which is larger than those reported for the copolymerization of CTC comonomers initiated by thiol^{3,4}. This difference may be connected with the non-CTC feature of the reaction system (refer to the diagram of copolymer composition).

The effect of monomer composition on the initial copolymerization rate has also been investigated. From Figure 3, we know that at the absence of MMA, R_{po} is equal to zero, namely thiol can not initiate the homopolymerization of AN. Alternatively, the homopolymerization of

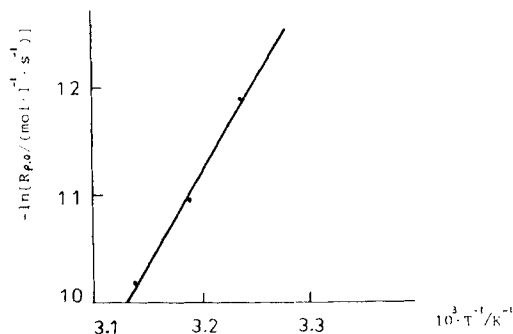


Figure 2, Arrhenius plot for the variation of R_{p0} with temperature T ;
 $[MMA]=[AN]=4.51\text{ mol/l}$, $[RSH]=6.84 \cdot 10^{-3}\text{ mol/l}$,
 solvent: methyl ethyl ketone.

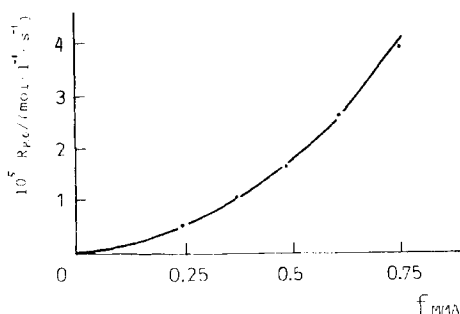
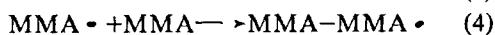


Figure 3, Relationship between initial copolymerization rate,
 R_{p0} and mole fraction of MMA in feed comonomer,
 f_{MMA} ; $[RSH]=3.42 \cdot 10^{-3}\text{ mol/l}$, $[MMA]+[AN]=9.02\text{ mol/l}$,
 solvent: methyl ethyl ketone, temp.: 40°C .

MMA can be induced by thiol. So the initiation reaction may be assumed to be



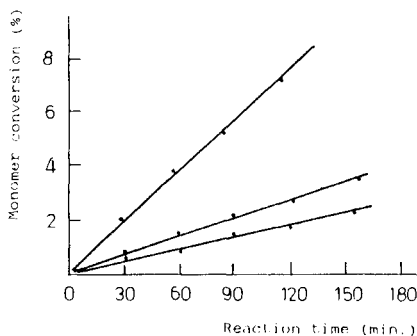


Figure 4, Plot of monomer conversion vs. reaction time;

[MMA]=[AN]=4.51 mol/l; [RSH]= $6.84 \cdot 10^{-3}$ mol/l; temp.: 40°C;

solvent: 1, N,N-dimethylacetamide, 2, methyl ethyl ketone, 3, benzene.

Because only MMA can accept a proton from thiol to produce the primary radicals, the more the fraction of MMA, the faster the copolymerization (see Figure 3).

N,N-dimethylacetamide (DMAc), methyl ethyl ketone (MEK) and benzene were chosen to test the influence of solvent on the copolymerization. Figure 4 indicates that DMAc is the most favourable solvent for the copolymerization, MEK takes the second place, and benzene is the third one. It is evident that the value of R_{po} is related to the polarity of the solvent. For most free radical polymerizations, the propagating species are not very solvent dependent unless some special conditions are established⁵. The effect of solvent on the copolymerization may be ascribed to the influence of solvent's polarity on reaction (1) shown above.

Effect of [RSH] on the molecular weight of poly(MMA-co-AN)

The influence of the concentration of RSH on the molecular weight of the resultant copolymer is shown in Figure 5. The plot of $1/\bar{M}_w$ vs. $[RSH]^{0.5}$ is linear, and the intercept is zero. The latter means that thiol is the only initiating source and monomer or solvent chain-transfer is absent.

Copolymer composition

The composition of the copolymer is determined by means of nitrogen elemental analysis. Copolymer composition and the respective comonomer

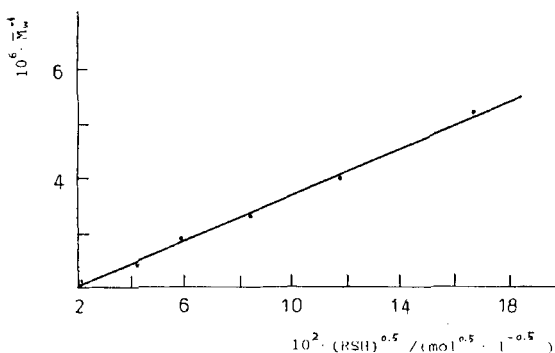


Figure 5, Plot of reciprocal weight-average molecular weight, \bar{M}_w^{-1} , vs. concentration of thiol, $[RSH]$, $[MMA]=[AN]=4.51\text{ mol/l}$, solvent: methyl ethyl ketone, temp.: 40°C .

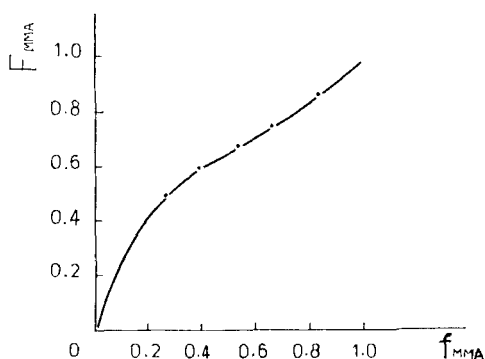


Figure 6, Copolymer composition diagram

(F_{MMA} , f_{MMA} : mole fraction of MMA in copolymer and feed, respectively),

$[MMA]+[AN]=9.02\text{ mol/l}$, $[RSH]=3.42 \cdot 10^{-3}\text{ mol/l}$,

solvent: methyl ethyl ketone, temp.: 40°C .

Table 1, Relationship between copolymer composition (F_{MMA}) and feed composition (f_{MMA})^{a)}

$f_{MMA} = \frac{[M_{MMA}]}{[M_{MMA}] + [M_{AN}]}$	0.25	0.38	0.50	0.63	0.75
$F_{MMA} = \frac{d[M_{MMA}]}{d[M_{MMA}] + d[M_{AN}]}$	0.48	0.58	0.66	0.74	0.81

a) $[RSH]=3.42 \cdot 10^{-3}\text{ mol/l}$, $[MMA]+[AN]=9.02\text{ mol/l}$, solvent: MEK, temp.: 40°C

feed composition are listed in Table 1. Figure 6 shows the relationship between F_{MMA} and f_{MMA} where F_{MMA} and f_{MMA} represent the mole fraction of MMA in copolymer and feed comonomer respectively. As we know that the copolymerization of CTC comonomer usually leads to the production of an alternative copolymer^{3,4}. However, the diagram of the copolymer composition in Figure 6 indicates that the resultant copolymer is not the alternative one. We may come to the conclusion that the copolymerization of MMA with AN initiated by thiol does not involve in the charge transfer complex.

In accordance with the data given in Table 1, the monomer reactivity ratios were calculated to be $r_{MMA} = 1.28 \pm 1$ and $r_{AN} = 0.18 \pm 1$ by the aid of the Yezrielev-Brokhina-Roskin method⁶, which approach to the classical values published in handbook⁷.

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