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Thermal terpolymerization of alphamethylstyrene, acrylonitrile and styrene

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Abstract

The ceiling temperature constraint encountered in the homopolymerization of alphamethylstyrene, AMS, can be circumvented by copolymerization with acrylonitrile to prepare multicomponent random microstructures that offer higher heat resistance than SAN. The feasibility of a thermal initiation of free radical chain polymerization is evaluated by the study of the terpolymerization kinetics of AMS–AN–Styrene. Process considerations such as polyrates, molecular weight of the copolymer formed, sensitivity of molecular weight, molecular weight distribution and kinetics to temperature are measured. The range of weight fractions of monomers of styrene, acrylonitrile and alphamethylstyrene varied in the study are $f_{sty} = 0.1–0.45$, $f_{an} = 0.1–0.4$, $f_{ams} = 0.2–0.75$, respectively. Empirical correlations are provided for the polyrate, weight average molecular weight, M_w, in the temperature range 398–418 K. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Alphamethylstyrene acrylonitrile; Styrene; Terpolymerization

1. Background

There is significant commercial interest in manufacturing multi component copolymers as indicated by the product literature of BASF and Bayer with alphamethylstyrene (AMS) as the primary monomer of choice. Products which offer higher heat resistance than SAN (styrene acrylonitrile) can be made by copolymerizing AMS with acrylonitrile (AN) thereby circumventing the ceiling temperature effect found in the homopolymerization of AMS. The ceiling temperature as indicated by Sawada [1] at atmospheric pressure for homopolymerization of AMS is 61°. Ceiling temperature is the temperature above which the depolymerization or reverse polymerization is preferred to the forward polymerization. Recently Sharma [2] presented the chain sequence distribution of the AMS–AN copolymer as geometric distribution and as a function of the monomer compositions and reactivity ratios, neglecting effects due to Markov second order statistics and used it to predict the potential for the formation of Grassie chromophores [3] in the copolymer. Here the need for control of the chain sequence distribution to improve product performance and ease of manufacturing was highlighted. One other method for control of the chain sequence distribution is the addition of a termonomer such as styrene. It would be desirable from product performance considerations such as heat resistance, color, etc. to add a termonomer to the AMS–AN copolymer. As pointed out by Shwier [4] f_{an}, the weight fraction of AN in the monomers has a dominant effect on the copolymerization kinetics of AMS–AN using standard free radical initiators. The effect of adding styrene as a termonomer on the polyrates and molecular weight of copolymer formed is not well understood with scarce data available in the literature. Further a thermal initiation method of free radical chain polymerization might further improve the product color and might offer commercial possibilities provided other process considerations such as polyrates, molecular weight of copolymer formed, sensitivity of molecular weight to temperature in the reactor, sensitivity of molecular weight distribution to reactor operating temperature are known. In this study terpolymerization kinetics of AMS–AN–STY using thermal initiation is provided. The range of weight fractions of monomers varied in the study are $f_{sty} = 0.1–0.45$, $f_{an} = 0.1–0.4$, $f_{ams} = 0.2–0.75$, for the weight fraction in the monomers of styrene, acrylonitrile, alphamethylstyrene respectively. Empirical correlations are

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Nomenclature

AMS	Alphamethylstyrene
AN	Acrylonitrile
E	Activation energy (kcal/mol)
f	Weight fraction
K	Pseudo first order rate constant (1/h)
M	Total monomer concentration (mol/l)
M_w	Molecular weight
R	Universal constant (kcal/mol K)
R_p	Polyrate (mol/l h)
STY	Styrene
T	Temperature (K)
Subscripts	
an	Acrylonitrile
ams	Alphamethylstyrene
sty	Styrene
o	Pre-exponential constant
w	weight averaged

provided for the polyrate, weight average molecular weight M_w, in the temperature range 398–418 K.

2. Experimental

Tube polymerization, free radical techniques where utilized to effect polymerization to small conversions. Sixteen different monomer compositions were used at three different temperatures, i.e. 398, 408 and 418 K. An oil bath was used to provide the constant temperature. The polymer when formed after 60 min at 398 K, 45 min at 408 K and 30 min at 418 K, was isolated by using precipitation methods, followed by drying and weighing. Details of the technique is provided in Shwier [4]. Part of the copolymer after drying was used to measure the number average molecular weight, M_n, weight average molecular weight, M_w, using gel permeation chromatography, GPC at the PASC at Monsanto, Indian Orchad, MA. The composition of the monomers used in the study along with the composition of the product formed, as calculated from the terpolymer monomer–polymer composition dependence equation provided by Odian [5], is provided in Table 1. The reactivity ratios used were the same as for those used for respective copolymerizations—AMS, 1; AN, 2; STY, 3; r_{12}, 0.1; r_{21}, 0.06; r_{13}, 0.3; r_{31}, 1.3; r_{23}, 0.04; r_{32}, 0.4. The polyrate was calculated by dividing the conversion, as measured by weight percent of polymer made by the time allowed for polymerization.

3. Results

A pseudo-first order rate expression was used to express the polyrate:

$$R_p \ (\text{mol/l h}) = K_0 \exp(-E/\mathrm{R}T)\{M\} \quad (1)$$

where M is the monomer concentration expressed in mol/l

$$K_o \exp(-E/\mathrm{R}T) = K.$$

This approach is suggested here in order to circumvent the need to quantify the mechanism of thermal initiation of styrene and/or alphamethylstyrene such as the reaction order of three as suggested in the literature [6–8].

The K value at a given temperature were calculated by regression with two independent variables, i.e. f_{an} and f_{sty} the weight fraction in the monomers of acrylonitrile and styrene respectively. Thus at 398 K, the following expression for K is obtained, with a $r^2 = 0.976$, standard error of estimate = 0.065 for 16 data points

$$K = 0.479 f_{an}^{0.706} f_{sty}^{0.292}. \quad (2)$$

In a similar fashion expressions for K were obtained at

Table 1
Monomer and polymer compositions of samples used in tube polymerization study

AMS (wt fraction)	AN (wt fraction)	STY (wt fraction)	AMS (wt fraction)	AN (wt fraction)	STY (wt fraction)
0.45	0.1	0.45	0.295	0.251	0.454
0.55	0.1	0.35	0.362	0.262	0.376
0.65	0.1	0.25	0.432	0.276	0.292
0.75	0.1	0.15	0.511	0.297	0.192
0.4	0.2	0.4	0.266	0.361	0.373
0.5	0.2	0.3	0.336	0.369	0.295
0.6	0.2	0.2	0.408	0.38	0.212
0.7	0.2	0.1	0.489	0.397	0.114
0.3	0.3	0.4	0.212	0.421	0.367
0.4	0.3	0.3	0.287	0.425	0.288
0.5	0.3	0.2	0.365	0.431	0.204
0.6	0.3	0.1	0.451	0.44	0.108
0.2	0.4	0.4	0.156	0.464	0.379
0.3	0.4	0.3	0.238	0.464	0.298
0.4	0.4	0.2	0.325	0.465	0.21
0.5	0.4	0.1	0.42	0.468	0.112

Table 2
C1 and C2 values in the rate expression for terpolymerization of AMS–AN–STY using thermal initiation methods

Temperature (K)	C1	C2
398	0.706	0.292
408	0.691	0.274
418	0.668	0.241

408 and 418 K

$$K = 0.836 f_{\mathrm{an}}^{0.694} f_{\mathrm{sty}}^{0.274} \qquad (3)$$

with coefficient of determination, $r^2, r^2 = 0.981$, standard error of estimate = 0.056 for $N = 16$ data points at 408 K

$$K = 1.384 f_{\mathrm{an}}^{0.668} f_{\mathrm{sty}}^{0.241} \qquad (4)$$

with $r^2 = 0.96$, standard error of estimate = 0.079 for $N = 16$ data points at 418 K.

A generalized expression for the polyrate was obtained by using the Arrhenius dependence of the first order pseudo rate constant

$$K = 2.1 \times 10^9 \exp(-8327.7/T) f_{\mathrm{an}}^{\mathrm{C1}} f_{\mathrm{sty}}^{\mathrm{C2}} \qquad (5)$$

the values for C1 and C2 obtained from the regression are given in Table 2. In order to illustrate the goodness of fit using an average values for C1 = 0.688 and C2 = 0.262, the experimental values are shown in Fig. 1 along with the regression line.

In a similar fashion a empirical relation for the weight average molecular weight of the polymer made was obtained

$$M_{\mathrm{w}} = 2.4 \times 10^{-7} \exp(7760/T) R_{\mathrm{p}}^{\mathrm{C3}} f_{\mathrm{ams}}^{\mathrm{C4}} \qquad (6)$$

The values of C3 and C4 obtained from the regression along with the statistics of the regression are provided in Table 3.

4. Conclusions

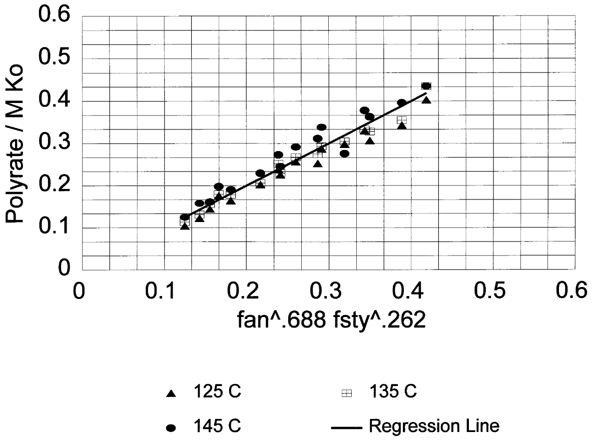

Fig. 1. Experimental values with the regression line for thermal terpolymerization of alphamethylstyrene acrylonitrile and styrene.

A pseudo first order rate expression was used to represent polyrate and molecular weight data for terpolymerization of AMS–AN–STY. The weight fraction AN in the monomers was the primary dominating variable on the polyrate and the weight fraction of styrene the secondary variable. The dependence of the polyrate on the weight fraction of AMS and AN changed little with temperature in the range of $398\ \mathrm{K} < T < 418\ \mathrm{K}$. The polyrate dependence on temperature was Arrhenius in nature. The weight averaged molecular weight M_{w} increased with the polyrate with roughly a square root dependence and was inversely proportional to the weight fraction AMS.

The dependence changed little with temperature in the range of $398\ \mathrm{K} < T < 418\ \mathrm{K}$. The molecular weight decreased with temperature with other things constant and the dependence on temperature was exponential. Further modeling from first principles may be needed to fully understand the nature of the interdependence in the terpolymerization kinetics. The polydispersity, i.e. a measure of the molecular weight distribution, $M_{\mathrm{w}}/M_{\mathrm{n}}$ was 1.843 averaged over the 48 data points with a standard deviation of 0.157.

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Table 3
C3, C4 values in the empirical relation for M_{w} in terpolymerization of AMS–AN–STY using thermal initiation methods

Temperature (K)	C3	C4	r^2	Standard error of estimate	N = number of data points
398	0.424	−0.392	0.991	0.033	16
408	0.434	−0.382	0.975	0.051	16
418	0.486	−0.281	0.999	0.019	16

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