

Influence of Curing Agent Concentration and Curing Temperatures on the Thermostability of Styrene–Acrylonitrile–Acrylamide–Trimethylolpropane Trimethacrylate Copolymer Systems

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Synopsis

Thermogravimetric (TGA) and infrared (IR) analyses were used to determine the thermal stability of a polymer system consisting of styrene–acrylonitrile–acrylamide–trimethylolpropane trimethacrylate. This study indicates that increases in curing temperature and the use of two initiators with different activities decreases the percentages of unreacted monomers. This increases the thermal stability of the polymer. To prove this, dynamic and isothermal TGA were used. The change in typical functional groups found by IR spectra also confirms this observation.

INTRODUCTION

A high-temperature copolymer consisting of styrene (St), acrylonitrile (ACN), and acrylamide (Aa) and crosslinked with trimethylolpropane trimethacrylate (TMPTMA) has been used with inorganic fillers (for example, silica sand and cement) to produce polymer concrete. These composites have exhibited high compressive strength (170–200 MPa) and durability to high-temperature (240°C) brines and steam.

One of the properties characterizing the polymer system is thermal stability, which means the ability of a material to maintain the required mechanical properties at a given temperature. There are two principal factors characterizing the thermal stability of polymer systems—physical and chemical. The physical conception of a thermally stable polymer is that it has a high melting or softening point. The use of many polymers is limited not only by the breaking of chemical bonds but rather by changes in physical characteristics at elevated temperatures. They maintain their chemical structure but at the same time become weak, soft, and finally fluid.

One of the ways to increase the melting point is by introduction of polar substituents such as CN and/or hydrogen-bonding groups such as NH_2 . Another way to increase the thermal stability is to increase the curing temperature when the molecular chain starts to grow, thereby enabling a three-dimensional structure to form. The ratio between the process temperature (T_{pr}) and glass transition temperature (T_{g}) is very important for choosing the region of the curing temperature. When $T_{\text{g}} > T_{\text{pr}}$, the curing terminates, and a high percentage of unreacted monomers remain in the system. When $T_{\text{pr}} > T_{\text{g}}$, complete curing takes place.

The curing of monomers containing unsaturated groups by a free-radical mechanism is highly dependent upon the selection of the curing agent. A quantitative estimate of the rate of curing can be made by determining the degree of conversion of the reactive groups. Therefore, the thermal stability of polymers can be estimated by thermal gravimetric and infrared analyses to determine the conversion of these groups.

EXPERIMENTAL

Materials and Test Methods

Materials used in this study are as follows: styrene (St), acrylonitrile (ACN), acrylamide (Aa), and trimethylolpropane trimethacrylate (TMPTMA). The physicochemical properties of these materials are summarized in Table I. The monomer system used for thermal gravimetric (TGA) and infrared spectra (IR) analyses was 55 wt. % St–35 wt. % ACN–5.0 wt. % Aa–5.0 wt. % TMPTMA. The curing agents for the polymerization of these monomers were azobisisobutyronitrile (AIBN) and di-*tert*-butyl peroxide (DTBP). Thermal polymerization was used to polymerize this system. A DuPont 990 thermal analyzer with a DuPont thermogravimetric plug-in cell module was used to determine the thermal stability of the polymer.

When used in the dynamic mode, TGA measures the loss of weight as a function of temperature. In these tests the samples were heated in a 80 cc/min nitrogen gas flow from room temperature to 500°C at a rate of 10°C/min.

TGA, when utilized in the isothermal mode, measures the loss of weight as a function of time at a constant temperature. The amount of residue after 4 hr of heating was determined.

Infrared spectroscopic analysis was performed using a Perkin–Elmer infrared spectrophotometer 297. The KBr pellet procedure was used for the IR analysis. A mixture of 200 mg KBr and 4 mg polymer, crushed to <0.104 mm, was packed into the special sample cup and evacuated to about 10^{-1} Torr for 8 to 10 min. After evacuation, the KBr–polymer mix was pressurized to 125–140 MPa for 4 to 5 min. The mix was then used to prepare 12.5-mm-diam. \times 0.125-mm-thick specimens.

TABLE I
Physicochemical Properties of Monomer Systems for High-Temperature PC Applications

Monomer	Structure	Molecular weight	Melting point, °C	Boiling point, °C	Flash point, °C	Condition
Styrene (St)	$C_6H_5CHCH_2$	104.14	–31	146	31.1	liquid
Acrylonitrile (ACN)	CH_2CHCN	53.06	–82	77.3	1.1	liquid
Acrylamide (Aa)	$CH_2CHCONH_2$	71.08	84.5	125	—	solid
Trimethylolpropane trimethacrylate	$(CH_2CCH_3-COOCH_2)_3-CCH_2CH_3$	338	—	—	>300	liquid

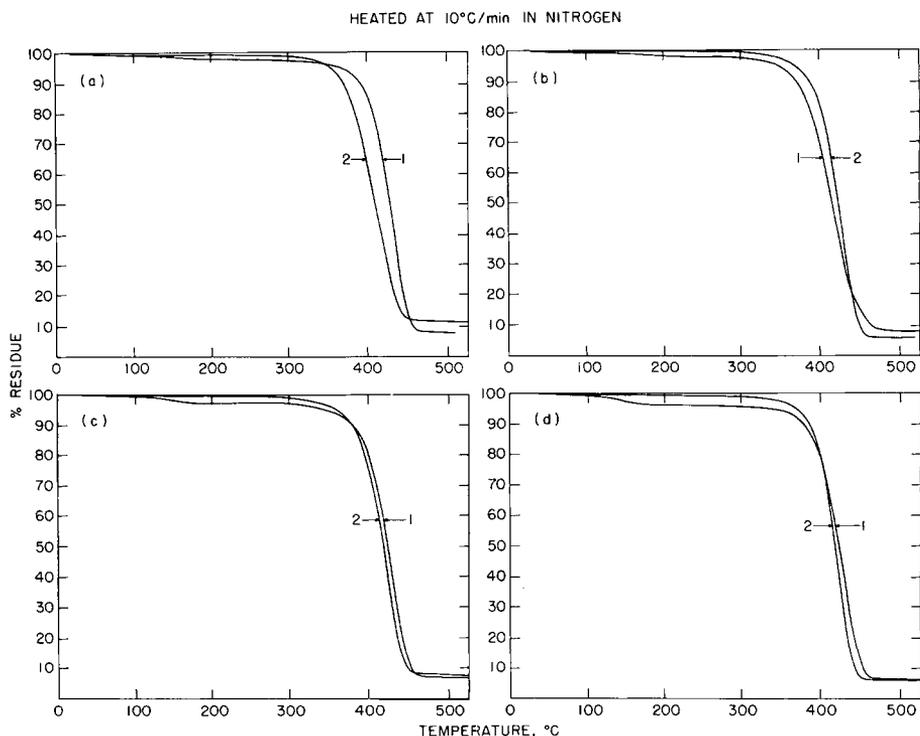


Fig. 1. Influence of curing temperature and curing agent on thermal properties of polymer. Monomer system: 55 wt. % styrene–35 wt. % acrylonitrile–5 wt. % acrylamide–5 wt. % trimethylolpropane trimethacrylate. (a) Curing temperatures 52 and 150°C, curing agent 0.5 wt. % AIBN; (b) curing temperatures 52 and 150°C, curing agents 0.5 wt. % AIBN + 0.5 wt. % DTBP; (c) curing temperatures 52 and 105°C, curing agents 0.5 wt. % AIBN + 0.5 wt. % DTBP; (d) curing temperatures 52 and 105°C, curing agent 0.5 wt. % AIBN.

Polymer Preparation

The monomer mixture, 55 wt. % St–35 wt. % ACN–5 wt. % Aa–5 wt. % TMPTMA, was heated in the temperature range 35 to 40°C to dissolve crystals of Aa. The curing agents AIBN and/or DTBP were then added. The polymer was obtained by use of a two-step curing procedure. The first step consisted of curing at 52°C. After this stage, which is called the induction period, the viscosity of the mixture is essentially the same; however, the system begins to lose its elasticity and solubility. When the temperature is subsequently increased to ~105 or 150°C (the second step), a polymer with a three-dimensional structure is obtained.

After the second step of curing was completed, the polymers were split into two parts. One part of the sample was used as a control, the other was washed in an excess of ethyl alcohol for 3 hr to dissolve any unreacted monomers. This part was then filtered in a Buchner funnel and the filtrate was saved for IR analysis. Both the control and the washed samples were dried in an oven at 100°C for 3 hr and then evaluated by TGA and IR. The filtrate was evaporated to dryness and TGA and IR spectra were also taken of the residue.

RESULTS

Figure 1 illustrates the results from thermogravimetric analysis performed in the dynamic mode. The data show the weight loss of polymer as a function of temperature for the polymers obtained at different curing temperatures (105 and 150°C) and different concentrations of free radical initiators (AIBN and a mixture of AIBN and DTBP). Curves 1 and 2 represent the TGA data for the polymer before and after washing in ethanol, respectively. As can be seen from Figure 1, polymer consisting of 55 wt. % St-35 wt. % ACN-5 wt. % Aa-5 wt. % TMPTMA loses weight at a temperature in the range 50 to 150°C. Increasing the curing temperature from 105 to 150°C by a second-step polymerization decreases the absolute value of the polymer weight loss from 2.7 wt. % at 105°C to 1.0 wt. % at a curing temperature 150°C. This is illustrated in curves 1, (a) and (d). Using a mixture of two initiators also results in a decrease in polymer weight loss. A comparison of the TGA curves in (c) and (d) with those in (a) and (b) indicates that, at the same curing temperature, the percent conversion of monomer to polymer is higher when a mixture of two initiators is used. On the basis of the assumption that variations in weight in the temperature range of 50 to 150°C are the result of the presence of unreacted monomers in the system, polymer samples were evaluated after washing in ethanol. These data, shown in Figure 1 as curve 2, indicate that after treatment with ethanol the polymers are less sensitive to the temperature change.

Data from the TGA when operated in the isothermal mode are given in Figure 2. This test measured the loss of weight as a function of time at a constant temperature of 250°C. It is shown that a more thermally stable polymer is produced after washing in alcohol. The stability is independent of curing temperature and initiator concentration. It was also found that polymers produced using only one curing agent but at higher curing temperatures are more stable with time and therefore have less weight change.

A quantitative estimate of the rate of cure for the polymers has been made using a vibrational spectroscopic method. In this method the degree of conversion and the reactive groups are utilized. Figures 3 to 6 indicate IR spectra

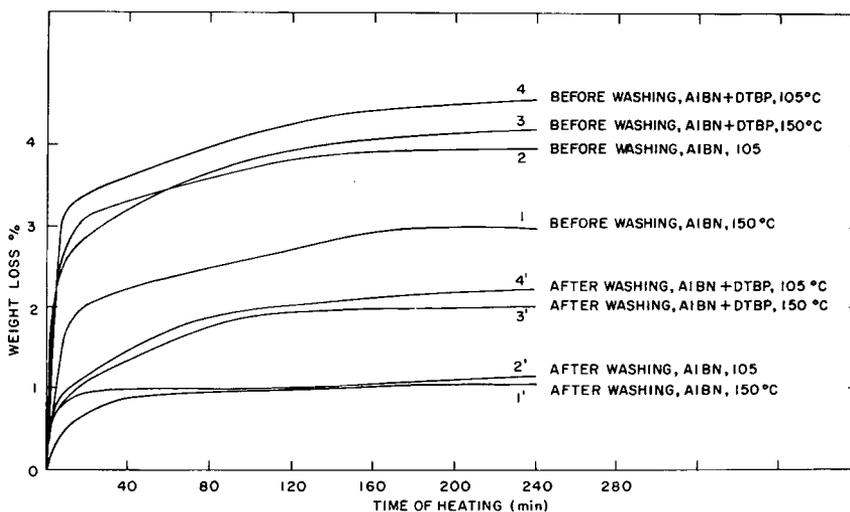


Fig. 2. Isothermal weight loss of polymer in nitrogen at 250°C.

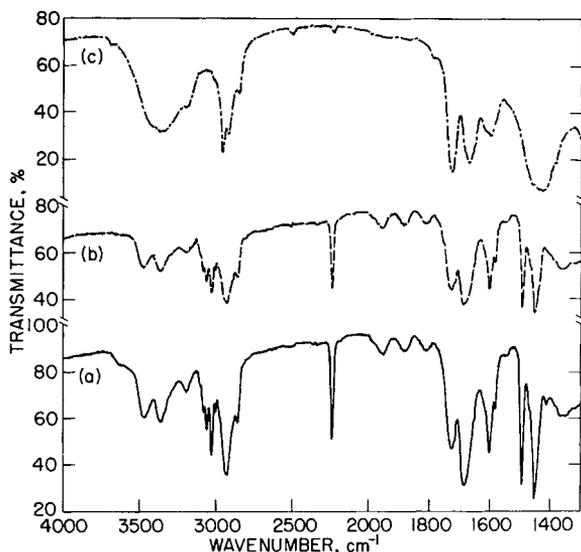


Fig. 3. Infrared spectra of St-ACN-Aa-TMPTMA copolymer. Initiator AIBN, curing temperatures 52 and 150°C. (a) Before washing in ethanol; (b) after washing in ethanol; (c) filtrate.

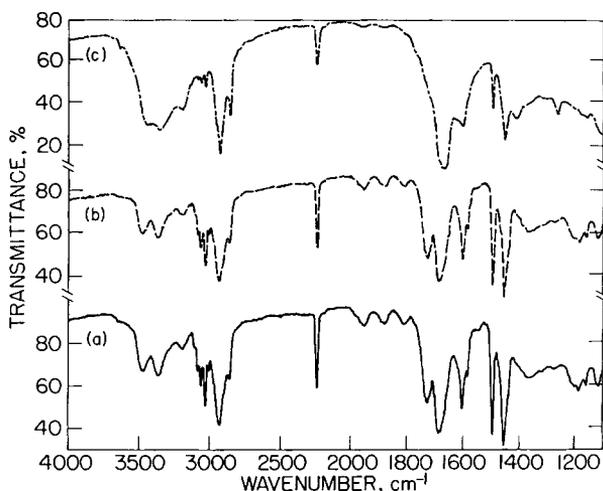


Fig. 4. Infrared spectra of St-ACN-Aa-TMPTMA copolymer. Initiators AIBN + DTBP, curing temperatures 52 and 150°C. (a)(b)(c) Same as in Fig. 3.

for polymers obtained at different curing temperatures and with different initiator concentrations. Spectra (a) deal with the polymers before washing in ethanol; spectra (b), after washing; and spectra (c), the filtrate after evacuation of the ethanol. Examination of the high-frequency range of IR spectra in the range of 3000 to 1400 cm^{-1} (Figs. 3 to 6) associated with the functional groups indicates a decrease in the absorption band of such functional groups as asymmetrical and symmetrical stretching vibration $-\text{CH}=\text{CH}_2$ groups (3030 cm^{-1}), asymmetrical stretching vibration CH_2- groups (2930 cm^{-1}), $\text{C}=\text{N}$ groups (2238 cm^{-1}), stretching vibration $-\text{C}=\text{O}$ groups (1730 cm^{-1}), CONH_2 groups (1679 cm^{-1}), benzene rings (1602 and 1498 cm^{-1}), and unsaturated $-\text{CH}_2-$ groups (1455 cm^{-1}). Table II gives the values of the absorption bands for the groups

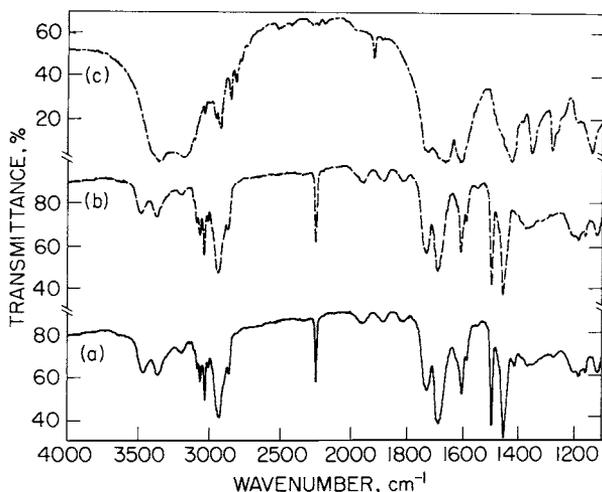


Fig. 5. Infrared spectra of St-ACN-Aa-TMPTMA copolymer. Initiator AIBN, curing temperatures 52 and 105°C. (a)(b)(c) Same as in Fig. 3.

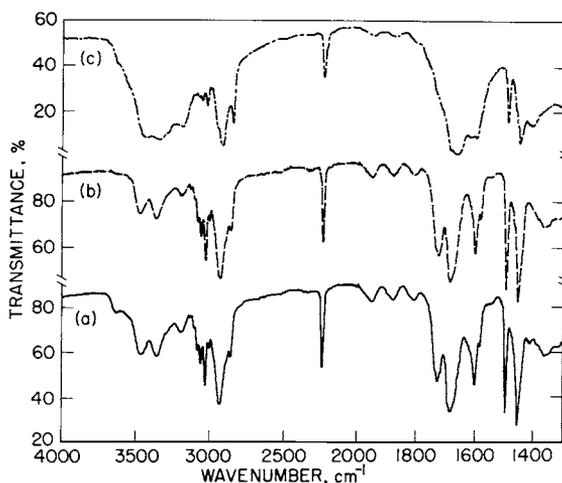


Fig. 6. Infrared spectra of St-ACN-Aa-TMPTMA copolymer. Initiators AIBN + DTBP, curing temperatures 52 and 105°C. (a)(b)(c) Same as in Fig. 3.

found in the polymers obtained at the specific conditions described by the four IR spectra.

When AIBN was used as a curing agent at the temperature of 105°C, the absorption peaks of such functional groups as unsaturated CH₂, benzene ring, CONH₂, and CN in the IR spectra of the filtrate are absent (Table II). At the same time, the value of the absorption band for the —CH=CH₂, —CH₂, and C=O groups were sufficiently high. Increasing the curing temperatures to 150°C increases the amount of monomer polymerized, as can be seen from the increased values of the absorption bands for the typical functional groups. When the mixture of initiators was used, the opposite effect can be seen (Figs. 3 and 4). Increasing the curing temperature leads to a decrease in the optical density of typical functional groups. Table II indicates that by using a mixture of two initiators at a curing temperature of 105°C, the intensity of the spectral line is

TABLE II
Summary of Results of IR Spectra Analysis for St-ACN-Aa-TMPTMA¹ Copolymer^a

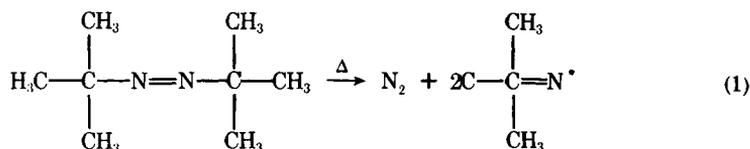
Functional group	Wave number cm ⁻¹	Absorption band × 10 ⁻¹											
		AIBN, 105°C			AIBN, 150°C			AIBN + DTBP, 105°C			AIBN + DTBP, 150°C		
		A	B	C	A	B	C	A	B	C	A	B	C
Asymmetrical & symmetrical stretching vibration of vinyl groups, -CH=CH ₂	3030	1.31	1.22	0.89	1.71	0.97	0.09	1.48	1.3	1.2	1.43	1.31	0.51
Asymmetrical stretching vibration	2930	2.03	1.86	2.41	2.6	1.46	0.9	2.45	1.97	7.16	2.21	2.04	2.94
-CH ₂ -	2238	1.88	1.85	0.1	2.6	2.4	0.1	2.21	1.85	1.92	2.05	1.93	1.15
C≡N	1730	1.33	1.33	0.03	1.74	1.27	5.62	1.57	1.31	0	1.39	1.38	0
Stretching vibration -C=O	1679	2.61	1.93	0	3.14	1.51	weak	2.59	2.16	weak	2.48	2.34	weak
CONH ₂	1602	1.37	1.33	0.9	1.82	1.38	0.15	1.59	1.38	0.45	1.53	1.53	0.11
Benzene ring	1498	3.38	2.86	0	4.24	2.74	0	3.71	3.11	3.8	3.3	3.3	0.02
Unsaturated -CH ₂ -	1455	3.68	3.16	0	4.59	2.60	0	4.07	3.46	5.35	3.78	3.74	0.3

^a St = Styrene; ACN = acrylonitrile; Aa = trimethylolpropane trimethacrylate; AIBN = azobisisobutyronitrile; DTBP = di-tert-butyl peroxide; A = polymer before washing; B = polymer after washing; C = filtrate after washing.

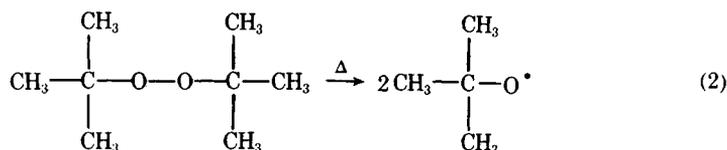
increased. At the curing temperature of 150°C, the intensity of the spectral line when only one initiator was used is higher than when the mixture of two initiators was used.

Discussion

In the investigations two initiators were utilized: azobisisobutyronitrile (AIBN) and di-*tert*-butyl peroxide (DTBP). The copolymerization reaction has been carried out in two steps. In the first step the temperature was maintained at 52°C. This temperature was chosen because AIBN is known to have a high rate of decomposition with the formation of free radicals, while the activation energy is low (~30 kcal/mol). The formation of free radicals takes place at 50 to 60°C. The kinetics of AIBN decomposition to free radicals has been studied and described in the literature.²⁻⁴ The reaction proceeds with the formation of nitrogen and dimethylcyanomethyl radicals which initiate the copolymerization reaction:



Qualitative enhancement of the free-radical source was in some cases achieved by addition of another initiator, DTBP. The decomposition of the latter proceeds via the thermal rupture of the O—O bond⁵ with the formation of *tert*-butoxy radicals:



It has been shown by Offenbach⁶ that the rate of decomposition of DTBP is slow and may be used most successfully at temperatures higher than 90°C, i.e., at temperatures where the rate of decomposition for AIBN is high. Table III shows the decomposition rates of the initiator which have been calculated for DTBP by the method of Bell⁵:

$$K (\text{sec}^{-1}) = 2.8 \times 10^{14} e^{-35000/RT}$$

and for AIBN by the method of Breitenbach⁷:

$$K (\text{sec}^{-1}) = 1.29 \times 10^{15} e^{-30500/RT}$$

TABLE III
Decomposition Rate Constant at Various Temperatures for Initiators AIBN and DTBP^a

Initiator	K, sec ⁻¹		
	55°C	105°C	150°C
AIBN	8.6 × 10 ⁻⁷	6.85 × 10 ⁻⁴	1.09 × 10 ⁻¹
DTBP	1.36 × 10 ⁻¹⁰	2.9 × 10 ⁻⁷	9.8 × 10 ⁻⁵

^a Calculated by the method of Bell⁵ and Breitenbach.⁷

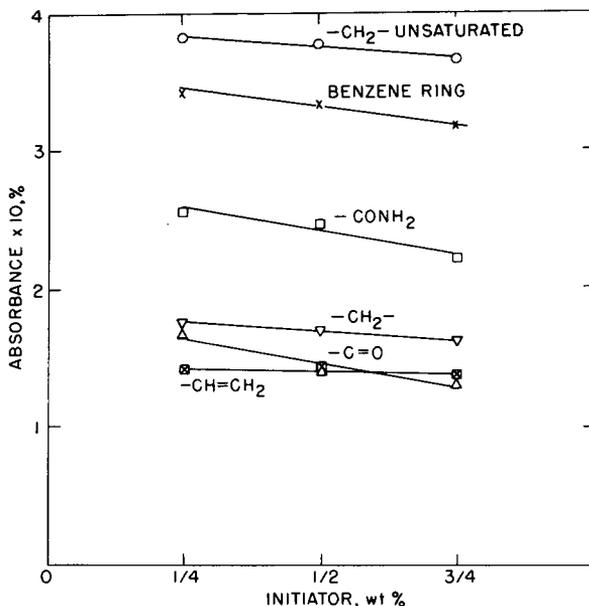


Fig. 7. Change in absorption band as function of initiator concentration.

The decomposition rates of the initiators at different temperatures (Table III) are in good agreement with absorption band data given in Table II. With the increase in the rate of decomposition of the initiator, the intensity of the absorption band of the typical function groups increases (Table II). Table II also indicates the tendency toward an increase in absorption. An opposite effect is observed when a mixture of two initiators is used at high temperatures. Table II clearly indicates that with an increase in the decomposition of the initiator, the absorption intensity decreases.

The results given in Tables II and III indicate that when AIBN is used alone, the rate of copolymerization increases with increased temperature. However, an increase in the rate of formation of active centers, coupled with an increase in the rate of chain propagation, leads to an increase in the overall rate of conversion of monomer to polymer. Simultaneously, termination reactions take place which partially slow down the process and shorten the length of the polymer. This leads to the formation of low molecular weight polymers (Table II).

Upon the removal of the unreacted monomers with ethanol, the absorption intensities of most of the functional groups decrease, which is consistent with the above proposed mechanism. However, since the rate of formation of active centers at high temperatures causes a significant increase in the rate of chain propagation (i.e., the activation energy for the formation of active centers is considerably higher than the activation energy of chain propagation), the percentage of low molecular weight products is negligible and has little influence on the properties of the polymer. These processes can be interpreted as follows: With the increase in the concentration of the initiator, the number of free radicals increases. This leads to a sharp increase in the number of active centers, which in turn causes an increase in the rate of chain termination. Consequently, at high initiator concentrations and high temperatures, there is a change in the ratio

of the reaction function between propagation and termination. The change in absorption intensity of characteristic groups as a function of the initiator concentration at 150°C is shown in Figure 7. It can be seen that an increase in the termination constant of the molecular chain (as measured by the decrease in the intensity of the absorption band) can be due to either the action of free-radical scavengers or competitive inhibitory action of one initiator versus the other.

Regardless of the actual mechanism, however, the results of this study have shown that the use of a mixture of two initiators and high temperature produces a higher yield of crosslinked polymer. This is an important factor in the successful formation of polymer concrete where the polymer system is the binder.

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