EXOTHERM CURVES: A METHOD FOR OBTAINING REPRODUCIBLE CURING PARAMETERS FOR RADIATION POLYMERIZATION OF VINYL-DIVINYL COMONOMERS[1]

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ABSTRACT

Polymerization parameters, suitable for both monitoring and comparative studies on catalytic and radiation polymerization of MMA/divinyl comonomers, are readily derived from time/temperature exotherm records. By geometric solution of exotherm curves Gel Effect Point (GEP), polymerization rate coefficients in Activation (PRC_i) and Acceleration (PRC_{ii}), and total dose (D) became available for kinetic studies. Individual components of the exotherm curve, such as reciprocal of time required to attain maximum on the exotherm curve, provide information on the overall rate of cure (ORC). Reciprocal of the time required to reach GEP characterizes the efficiency of cross-linking agents to cause onset of the gel effect phenomena in comonomer systems.

Repeated measurements and statistical analyses of such data, derived from exotherms, show good reproducibility and a high degree of reliability, especially with systems exhibiting rather sharp maxima on the exotherm curve.

Additional keywords: Polymerization, exotherm curves, activation period, acceleration period, gel effect point, cure, methyl methacrylate, divinyl monomer.

INTRODUCTION

Control and rate measurements of monomer polymerization become especially difficult at high conversion rates in bulk polymerization and when the monomers are used as saturants for laminates and other practical products. Until now, considerable uncertainty has been experienced in producing fully cured wood-polymer,

paper-polymer composites, and thin polymer films. In spite of all precautions, traces and the availability of oxygen in product-monomer systems (or absorbed oxygen in the purified monomer) were found to influence the time required for the onset of polymerization (known as inhibition and retardation periods) (Straforelli 1973), thus making the initial rates of conversion negligibly low. The net effect of inhibition is extension of the actual time required to full conversion. In practice the actual state of monomer conversion has been unknown, and irradiations were continued until no detectable monomer odor was given off by the product, on a trial and error basis.

Needless to say, such empirical control of monomer conversion does not lend itself well to experiments where a high degree of reproducibility is desired. This lack of control is in fact responsible (in part) for the widely varying dose requirements re-

ported for methyl methacrylate (MMA) (0.75 to 2.5 Mrad) and other monomers in the wood and paper polymer composite literature (Davies et al. 1969; Siau et al. 1965).

The classical polymer characterization techniques, used for assessing precise kinetic constants of steady-state polymerizations, such as precipitation and gravimetry, molecular weight determination by either osmometry, light scattering, ultracentrifuge, sedimentation, viscometry or dilatometry (Stille 1962), are not only too involved but can be used only at low levels of conversion (up to 10%). Furthermore, these methods are destructive in the sense that solutions of the polymers have to be produced in order to carry out these measurements. Such a procedure may pose a formidable task with polymers grafted to already existing polymer backbones (such as cellulose and lignin in case of wood and paper), and copolymers having thermoset properties. For these reasons values of monomer conversion were expressed in terms of polymer loading following evaporation of the unpolymerized monomer (Siau 1968; Kent 1964). From these measurements, however, no information is derived with respect to the actual degree of conversion.

It is a characteristic of free radical polymerizations that reactions proceed with the evolution of heat. The exothermal conditions culminate in a maximum, at which time the polymerization process is essentially complete with only an insignificant amount of unreacted monomer trapped in the polymeric network. The exotherm maximum was described by Oleesky and Mohr (1964) and by Schildknecht (1956). In wood polymer composite work, exotherm plots (temperature-time plots) were first introduced by Beall et al. (1966), who used these measurements to discern curing rate differences, anticipated with direct and radio-frequency heating in thermal decomposition of peroxide catalysts for the polymerization of vinyl monomers. The same technique was used by Davies et al. (1969), Kenaga (1970), and Pesek et al.

(1969). Davies et al. (1969), in accordance with Beall and coworkers (1966), divided the exothermic curve into three kinetically important stages (the initial stage in Beall et al.'s [1966] classification applies only to the heat/catalyst system for the case when the peroxide is added to the system prior to raising the system temperature to the ambient reaction temperature) namely:

I. Slow temperature rise, during which the inhibitors are destroyed (Induction Period, I);

II. Rapid temperature rise, during which most of the polymerization occurs (Exotherm Stage, II);

III. Cooling stage, during which heat dissipation occurs to the system and the polymerization is essentially complete.

The significance of these stages in polymerization was reiterated recently by Duran and Meyer (1972) in an effort to study the actual temperature rise in wood-monomer systems, produced during copolymerization of methyl methacrylate with a trifunctional cross-linking agent (trimethylol trimethacrylate), in basswood. In such studies the assumption is made that the polymerization rate relates to heat evolution from a given amount of monomer as controlled only by the rate at which the polymerization initiating free radical species was generated.

Earlier studies on bulk polymerization of new monomer systems, applicable to formulating improved wood and paper polymer composites, showed the usefulness of exotherm recordings to monitor the curing rates of cross-linked systems (Paszner 1970). The need for methods of assessing the critical polymerization parameters became quite obvious in an effort to quantify the observed differences in polymerization rates before and after gelation. Further, reproducibility of data was of importance in examining the basic hypothesis of the research program at large, i.e., that radiation polymerization of vinyl monomers may be accelerated by forming gelled three-dimensional networks. Such poly-

merization techniques were assumed to provide the handle through which elementary steps of the polymerization reaction (mainly propagation and termination) could be moderated or adjusted. On that basis characteristics of exotherm curves were intensively studied. The purpose of this paper is to describe a method of deriving critical polymerization parameters on which kinetic or qualitative judgments can be based.

MATERIALS AND METHODS

In all experiments reported here, 5-ml portions of methyl methacrylate (MMA)—tetraethylene glycol dimethacrylate (TEGDMA) comonomer mixture (vol/vol) were placed in small glass vials, which were sealed in a nitrogen atmosphere with rubber stoppers. Purification of the monomers was omitted since numerous preliminary radiation polymerization studies showed no inhibition periods on exotherm curves derived with either of the monomers used herewith. The exotherm curves of purified monomers were identical to those of the unpurified experimental material. The radiation polymerization was done in a Gammacell 220 at a dose rate of 0.812 Mrad/hr as determined by the Fricke dosimetry method (Cho 1970). The vials and contents were first conditioned to the ambient Gammacell chamber temperature (36 C) in irradiation position set in a styrofoam seat, which provided reproducible thermal conditions and positions within the chamber. In each case, the released exothermic heat of polymerization was measured with inserted copper-constantan thermocouples with signal sent to a time base strip chart recorder, calibrated against an ice-water reference junction. This technique, as previously described in detail by Davies et al. (1969), makes the assumption that polymerization rate relates to heat evolution and that such comparisons may be used between monomer systems.

Reproducibility of critical polymerization parameters, as derived from exotherm recordings by analysis of the exotherm curves
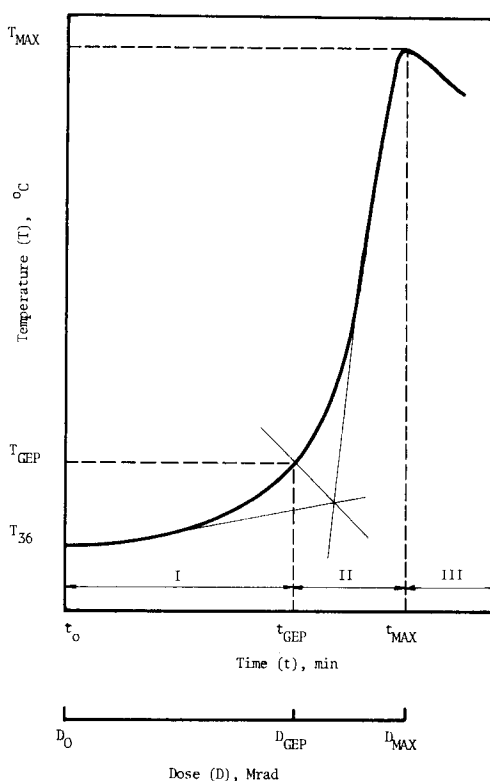

FIG. 1. Solution of a typical polymerization exotherm curve, including derivation of "Gel Effect Point" (GEP), "Cure" (MAX), and showing "Activation" (I) and "Acceleration" (II) periods.

(Fig. 1), was estimated on two comonomer systems composed of methyl methacrylate (MMA) and a divinyl compound (tetraethylene glycol dimethacrylate, TEGDMA) of 95:5 and 70:30 (vol/vol) mixing ratios, respectively. Nine runs of each mixture were made with identically prepared sample mixtures and carefully controlled irradiation conditions. The replicate exotherm curves were analyzed for the critical polymerization parameters by three independent operators. Using these data, appropriate standard deviations and medians were calculated to assess the variability of these critical parameters caused by changing operators. Furthermore, on the basis of these data, the necessary number of replicate samples was calculated for the cases when the acceptable errors were ±1

TABLE 1. *Polymerization parameters, derived from exotherm curves, for the 95:5 MMA-TEGDMA comonomer system (E_I series)*

Observation	Operator	GEP		MAX		Polymerization rate coefficients °C/min	
		t_{GEP} min	T_{GEP} °C	t_{MAX} min	T_{MAX} °C	PRC_I	PRC_{II}
1	1	46.5	59			0.49	9.1
	2	46.0	59	56.5	150	0.50	8.6
	3	46.0	59			0.50	8.6
2	1	47.5	59			0.48	9.3
	2	47.0	59	57.5	152	0.48	8.9
	3	47.0	59			0.48	8.9
3	1	47.0	61			0.53	9.3
	2	46.0	60	57.0	154	0.53	8.5
	3	47.0	61			0.52	9.3
4	1	45.0	60			0.53	9.7
	2	44.5	59	54.5	152	0.51	9.3
	3	45.0	60			0.53	9.7
5	1	45.0	61			0.55	8.6
	2	44.0	59	55.5	151	0.52	8.0
	3	45.0	61			0.55	8.6
6	1	47.0	61			0.53	9.1
	2	46.0	59	58.0	161	0.50	8.5
	3	47.0	62			0.55	9.0
7	1	47.0	61			0.53	9.0
	2	46.0	59	57.5	156	0.50	8.4
	3	47.0	61			0.53	9.0
8	1	44.5	60			0.53	9.6
	2	44.0	59	54.5	156	0.52	9.2
	3	44.5	60			0.53	9.6
9	1	45.5	61			0.54	8.3
	2	47.0	60	57.0	156	0.51	9.6
	3	45.5	60			0.52	8.3

and ±0.5 for times (t) and 3 and 1 C for the temperatures observed.

RESULTS AND DISCUSSION

An idealized radiation polymerization exotherm curve, characteristic of MMA-divinyl cross-linked comonomers, is given in Fig. 1. The three basic stages of the radiation polymerization process are clearly evident in this time-temperature record. The stages of slow temperature rise (I), rapid temperature rise (II), and cooling (III) contain general characteristics of the curing process by radiation. As is evident in this figure, Duran and Meyer's (1972) and Beall et al.'s (1966) first stage, inhibition, a characteristic stage of polymerization of unpurified monomer by the

TABLE 2. *Polymerization parameters, derived from exotherm curves, for the 70:30 MMA-TEGDMA comonomer system (E_2 series)*

Observation	Operator	GEP		MAX		Polymerization rate coefficients °C/min	
		t_{GEP} min	T_{GEP} °C	t_{MAX} min	T_{MAX} °C	PRC_I	PRC_{II}
1	1	19.5	69			1.7	16.0
	2	19.5	68	24.0	141	1.6	16.2
	3	19.0	66			1.6	15.0
2	1	19.5	69			1.7	15.0
	2	19.0	72	24.5	144	1.9	13.9
	3	18.5	71			1.9	12.2
3	1	19.0	68			1.7	14.5
	2	19.0	68	24.5	148	1.7	14.5
	3	18.0	68			1.8	12.3
4	1	18.0	67			1.7	13.2
	2	18.5	69	24.0	146	1.8	14.0
	3	19.0	68			1.7	15.6
5	1	17.5	70			1.9	13.3
	2	18.5	74	23.5	150	2.0	15.2
	3	18.0	72			2.0	14.2
6	1	17.5	70			1.9	14.2
	2	17.5	70	23.0	148	1.9	14.2
	3	17.5	70			1.9	14.2
7	1	17.0	64			1.6	12.3
	2	19.0	68	23.0	138	1.7	12.5
	3	18.0	68			1.8	14.0
8	1	18.5	66			1.6	13.4
	2	19.0	67	24.0	139	1.6	14.4
	3	18.5	66			1.6	13.2
9	1	17.0	68			1.9	15.3
	2	17.5	68	21.5	137	1.8	17.2
	3	17.5	69			1.9	17.0

heat/catalyst system, is practically absent in accelerated radiation polymerization. Contrary to normal experiences with heat/catalyst curing systems, the effects of usual inhibitor concentrations (20 to 40 ppm in MMA and 70 ppm in TEGDMA) were totally undetectable on any of the polymerization stages during accelerated radiation polymerization of vinyl/divinyl co-monomer systems. The cooling stage (III) is essentially without consequence from a polymerization kinetics point of view.

Kinetically only the first two stages are important:

1. Slow temperature rise, characterizing the Activation Period (I); and
2. Rapid temperature rise, called the Acceleration Period (II).

TABLE 3. *Calculated standard deviations, medians, and necessary number of replications of polymerization parameters for the E_1 series*

Factor [a]	Operator	t_{GEP} min	T_{GEP} °C	t_{MAX} min	T_{MAX} °C
Standard Deviation	1	1.11	0.87	--	--
	2	1.17	0.44	1.31	3.2
	3	1.03	1.00	--	--
Median	1	46.5	61	--	--
	2	46.0	59	57.0	154
	3	46.0	60	--	--
Necessary Number of Replicates (Error)		±1 min 7	$\pm3°$ 2	±1 min 4	$\pm3°$ 8
		$\pm.5$ min 21	$\pm1°$ 6	$\pm.5$ min 13	$\pm1°$ 40

[a] Number of observations N=9

Initiation, or the stage of slow temperature rise, is the only stage truly affected by radiation as it contributes significantly to the dose rate dependence of radiation polymerization.

Thus, under unaerobic conditions, in the beginning of the radiation polymerization reaction (I), the temperature rises linearly with time from the ambient Gammacell chamber temperature (36 C). This part of the polymerization process is identical with the steady-state stage of polymerization and is characteristic of all vinyl monomers polymerized under bulk conditions. The polymerization rate during this stage is proportional to the square root of the rate of free radical initiation, whereby it is dependent on the dose rate of radiation. For a mixture of compounds, irradiated by gamma rays, the absorbed dose becomes proportional to the sum of the components present and the weighted mass energy absorption coefficient derived for the component mixture.

Following the Activation Period (I), the rate of change of reaction temperature deviates considerably from linearity and increases at an accelerated rate to a well-defined exotherm maximum (Fig. 1). During this Acceleration Period (II), the overall polymerization rate increases because of the gel effect phenomena. Ac-

celeration actually arises as a result of decreased termination reaction in the highly viscous and partly cross-linked medium. The overall reaction rate (ORC) during this stage is thus proportional to the ratio of propagation (k_p) and square root of termination (k_t) rate constants: $ORC = k_p/k_t^{1/2}$

Considering the above two stages, the temperature (T, °C) versus time (t, min) data provide the following detailed polymerization characteristics (Fig. 1, Tables 1 and 2):

1. Initial conditions of the systems: (T_{36}, t_o).
2. Gel Effect Point (GEP): by geometric solution as the exotherm curve intersection by the perpendicular through a common point obtained by extrapolating the early and late curve stages. The estimated components of GEP are: T_{GEP} and t_{GEP}.
3. Exotherm maximum with components: T_{max}, and t_{max}.
4. Activation Period (I): the time interval to reach GEP, calculated as: $(t_{GEP} - t_o)$.
5. Acceleration Period (II): the time interval between GEP and the exotherm maximum and calculated as $(t_{max} - t_{GEP})$.

TABLE 4. *Calculated standard deviations, medians, and necessary number of replications of polymerization parameters for the E_2 series*

Factor[a]	Operator	t_{GEP} min	T_{GEP} °C	t_{MAX} min	T_{MAX} °C
Standard Deviation	1	1.00	1.96	--	--
	2	0.70	2.29	0.95	4.85
	3	0.56	2.06	--	--
Median	1	18.0	68	--	--
	2	19.0	68	24.0	144
	3	18.0	68	--	--
Necessary Number of Replicates (Error)		±1 min 5	±3° | 5	±1 min | 6	±3° | 7
		±.5 min 12	±1° | 20	±.5 min | 17	±1° | 35

[a] *Number of observations N=9*

As shown also in Fig. 1, dose (D) may be substituted for time (t) by using the appropriate dose rate factor, thereby describing radiation requirements at the single dose rate applied. These parameters fully characterize the polymerization process of vinyl monomer systems that exhibit a well-defined maximum exotherm at near complete conversion to polymer. Besides providing a visual, continuous, and permanent record of the reaction, the exotherm curve allows quantification of parameters of importance in comparing the polymerization behaviour of monomer systems studied under identical or comparable conditions.

Furthermore, the accelerating ability of divinyl monomer components in copolymerization can be derived from polymerization rate coefficients (PRC) as determined from data on Activation Period (I) (PRC_I) and Acceleration Period (II) (PRC_{II}). The polymerization rate coefficients, PRC_I and PRC_{II}, may be calculated for a particular set of exotherm data as ratios of partial differential temperatures and times required for activation (I) and acceleration (II), respectively.

$$PRC_I = (T_{GEP} - T_{36})/(t_{GEP} - t_o)$$
$$PRC_{II} = (T_{max} - T_{GEP})/(t_{max} - t_{GEP})$$

For example, in case of the 95:5 mixture of MMA:TEGDMA (Series E_1, Table 1) the calculated average curing rate before gelation (PRC_I) was 1.8 and that of PRC_{II} (rate coefficient of acceleration) 15.5. Similarly, in case of the 70:30 MMA: TEGDMA mixture (Series E_2, Table 2) the appropriate averages were 0.52 and 9.0, respectively. These differences in curing rates indicate practical and economic aspects of time measurements to GEP and T_{max} and directly determine the usefulness and proportion of cross-linking agent required as accelerator for a particular vinyl and possibly other type polymerization. The ratio of these polymerization rate coefficients (PRC_{II}/PRC_I) numerically expresses the increase in curing rate due to the accelerated gelation, which can be brought about in any particular comonomer system. This ratio was found to be an excellent numerical indicator of the increased polymerization rate due to the gel effect phenomena (Micko 1973).

The polymerization rate coefficients, although important in the quantification of different curing rates that occur before and after GEP, do not characterize the overall curing rate of the polymerization reaction or the rate of gelation of a particular system. These parameters, which now relate the structure and particular concentration of the cross-linking agent used, may be com-

piled by location of the time to maximum and time to reach GEP on the exotherm curve. Thus the reciprocal of the time required to attain maximum on the exotherm curve can be used advantageously in comparisons as a measure of the overall rate of cure (ORC $= 1/t_{max}$). By analogy, the reciprocal of the time to reach GEP ($1/t_{GEP}$) refers to the overall gelation rate and characterizes the efficiency of the cross-linking agent to cause onset of the gel effect phenomena.

The overall curing rate (ORC) is a kinetic parameter that characterizes the overall acceleration efficiency of a cross-linking agent in a particular comonomer system. It can also be viewed as an index of the acceleration efficiency of the cross-linking agent at different concentration levels in the same system. Such data can be readily derived from a series of mixtures containing varying proportions of cross-linking agent.

On examination of the average polymerization parameters in Tables 3 and 4, it is found that the median t_{max} values for the series E_2 (70:30 MMA:TEGDMA) and E_1 (95:5 MMA:TEGDMA) runs give ORC values of 4.17×10^{-2} min^{-1} (1/24), and 1.75×10^{-2} min^{-1} (1/57). It is surprising that a six-fold increase in TEGDMA concentration (from 5% to 30%) resulted in only a two-fold increase of ORC. Explanation of this phenomenon seems to lie with the diffusion controlled propagation rate found in highly cross-linked networks. The higher cross-linker concentration in the 70:30 mixture becomes a diffusion barrier to chain propagation and thus affects the overall rate of cure. As found earlier (Micko 1973), the accelerating ability of TEGDMA, as measured by ORC, is proportional to the cross-linking agent concentration only within the 0 to 10% concentration range. Outside this range increasing amounts of TEGDMA become less effective. This important observation is useful not only in setting practical limits to accelerated polymerization, but most of all allows for considerable savings in monomer costs. Running such concentration

series and evaluation of the above critical curing parameters provide means for double economy. The true significance of these parameters for accelerated polymerization in vinyl-divinyl comonomer mixtures is fully realized when a choice between available accelerating agents (di-, tri-, tetra- and multifunctional) must be made.

Reproducibility of the critical parameters just described is demonstrated on n = 9 replicate runs in Tables 1 and 2, with summary of the statistical analyses in Tables 3 and 4. Even the two parameters, derived by a somewhat arbitrary solution of GEP in Fig. 1 (with components t_{GEP} and T_{GEP}), are reproducible by different operators to a satisfactory degree. Replicate calculations indicate 5 to 7 as a satisfactory number of replicate samples when the acceptable errors are ± 1 min and 3 C. Only if a high degree of reproducibility (± 0.5 min) is required does the necessary number of replicate determinations become excessive [approximately 12 (E_2 Series) and 21 (E_1 Series)]. The data also indicate that the higher the maximum exotherm temperature, the better the reproducibility of the data between similar runs under carefully controlled irradiation (curing) conditions. This phenomenon seems to relate to the sharpness of the exotherm peak.

CONCLUSIONS

Polymerization exotherm records were found to provide useful data in deriving critical curing parameters for vinyl-divinyl comonomer systems. An arbitrary method for assessment of these parameters related to gelation (GEP) as well as cure (represented by the exotherm maximum) completely eliminates the guesswork in determining when a particular sample reaches the theoretically cured stage. Statistical analysis on the individual parameters indicates good reproducibility between runs and operators assigned to evaluating the data. Only 5 to 7 replicate runs seemed to be necessary when the acceptable level of error was set at ± 1 min and ± 3 C.

Beyond this advantage the basic informa-

tion available from the exotherm curve with respect to GEP, Activation Period (I), and Acceleration Period (II) provides important parameters in evaluating efficiencies of cross-linking agents. The particular sensitivities of PRC values lend themselves well for quick sorting among activators and/or accelerators used in radiation copolymerization studies. Further, plots of PRC ratios or overall rate constants (ORC) against the particular accelerator concentration could be used for assessment of the optimum cross-linking agent concentration that is both effective and economical. Such plots also provide decisive information in comparing cross-linking agents with widely varying degrees of reactivity.

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