

Thermal Analysis of Styrene-Alkyl Methacrylate Polymers. II. Thermogravimetric Kinetics

WALTER Y. WEN, *Honeywell Inc., Plastic Materials and Processing
Laboratory, Hopkins, Minnesota 55343*, and JACOB W. LIN, *Honeywell
Inc., Corporate Material Sciences Center, Bloomington,
Minnesota 55420*

Synopsis

The thermal stability and degradation kinetics of several polystyrenes and styrene-alkyl methacrylate copolymers and terpolymers with a number-average molecular weight (\bar{M}_n) of 6000–250,000 g/mole have been studied using dynamic thermogravimetry (TG). The degradation kinetics of each polymer sample have been successfully attributed to a simple first-order reaction expression. The results indicate that the thermal stability and degradation kinetics of the polymers are independent of the size of the molecules within the molecular weight range investigated. The steric hindrance effects of the pendent groups appear to be responsible for the improved thermal stability and resistance of C—C bond scission in the styrene-alkyl methacrylate copolymers and terpolymers.

INTRODUCTION

As pointed out in the preceding paper,¹ a holographic recording thermoplastic for practical purposes must be durable under thousands of read-erase cycles involving repeated heating and cooling. If the material is to respond reproducibly over a large number of the holographic operation cycles, a prime requirement is that it must be thermally stable against degradation. A previous investigation² indicates that the thermal stability and degradation kinetics of thermoplastics are essential information for the development of new holographic media. Through glass transition temperature (T_g) measurements, the side-group effects on the transition phenomena of styrene-alkyl methacrylate copolymers and terpolymers have been identified.¹ Thermal degradation kinetic studies on these polymers provide a deeper insight into the steric effects contributed by the various pendent groups on the thermal stability of the materials. The T_g and thermal stability of a thermoplastic apparently are the two preliminary characteristics determining the applicability of the material as an effective holographic recording medium.

Because the goal of the present studies is holographic recording thermoplastics, only those copolymers and terpolymers of styrene-alkyl methacrylates that have been identified as potential holographic materials¹ were selected in the kinetic measurements. In this investigation the technique of dynamic thermogravimetry (TG) was employed to monitor the change of sample weight under a linear heating process. The technique of isothermal TG was not pursued because the information obtained by dynamic TG apparently has satisfied the specific requirement for characterizing holographic memory thermoplastics.

EXPERIMENTAL

The copolymers and terpolymers of styrene with ethyl methacrylate (EMA), hexyl methacrylate (HMA), octyl methacrylate (OMA), decyl methacrylate (DMA), and octadecyl methacrylate (ODMA) with different \bar{M}_n values as indicated in the preceding paper¹ were included in the present analysis. Several samples of atactic and isotactic polystyrenes also were tested for comparison. The samples studied are tabulated in Table I.

Details of the sample preparation have been described before.¹ All of these polymer samples had been characterized by UV-IR spectroscopy techniques, their molecular weight distribution (MWD) determined by gel permeation chromatography (GPC), and their T_g 's determined by differential scanning calorimetry (DSC) and thermomechanical analysis (TMA).¹

A Cahn (Ventron Instrument Corp.) electrobalance with a Perkin-Elmer furnace and a Model UU-1 programmer was used in the dynamic TG analysis to monitor the weight loss kinetics of a sample during heating. A polymer solid sample of 2-3 mg was loaded into an aluminum crucible which was heated in a steady flow of dry nitrogen gas at 5°C/min from ambient to 600°C where the weight loss process was practically 100% completed as indicated in the typical TG curves shown in Figure 1. The sample temperature was measured by a Chromel-Alumel thermocouple located immediately above but not in touch with the sample or the sample container.

The output signals from the TG analyzer were fed into a Honeywell H112 minicomputer interface where the data were converted into binary digits and stored in the computer memory. Details of this computer-aided data acquisition system have been reported recently.³ The data obtained from a TG analysis were punched in a paper tape which was processed on a time-sharing terminal of a Honeywell Computer Network (HCN) system where different FORTRAN programs for specific calculations were stored.

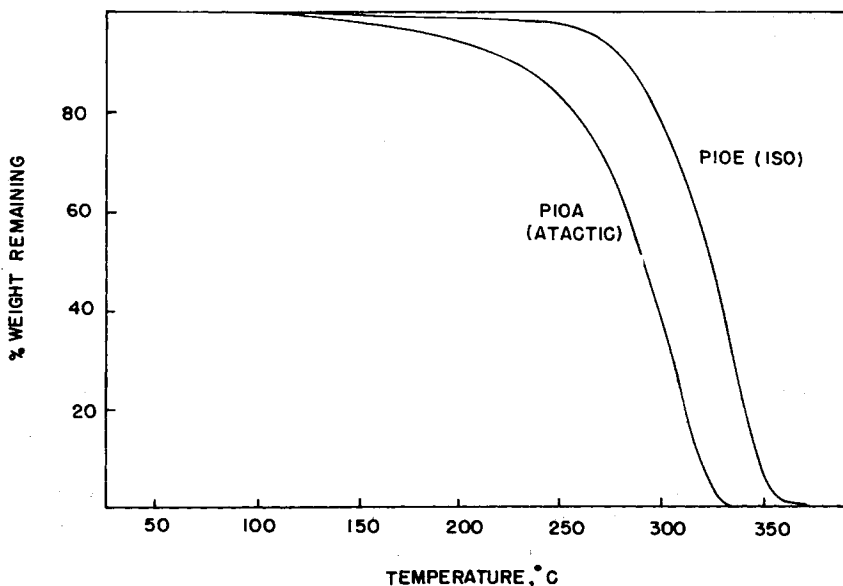


Fig. 1. Curves of dynamic thermogravimetric analysis of isotactic and atactic polystyrene as measured at a heating rate of 5°C/min in a steady flow of dry nitrogen gas.

TABLE I
Results of Thermal Stability and Degradation Kinetics of Various Styrene-Alkyl Methacrylate Copolymers and Terpolymers As Determined by Dynamic Thermogravimetry at 5°C/min Heating Rate in Dry Nitrogen

Sample	Type	Monomer ^a	Monomer Feed Mole %	\bar{M}_n	IPDT, °C	% Conversion	Initial Rate ^b		E_a , kcal/mole	A./sec
							Reaction/ Sec	10 ⁻⁶ %		
P10B	Homopolymer (Atactic)	"	—	33,000	—	10-80	6.6	27.6	7.08 × 10 ⁷	
P10C	Homopolymer	"	—	33,000	340	10-95	8.8	27.6	7.08 × 10 ⁷	
P10D	Homopolymer	"	—	250,000	341	15-99	7.1	26.8	1.74 × 10 ⁷	
P10E	Homopolymer (Isotactic)	"	—	—	344	2-99	9.4	36.8	1.03 × 10 ¹¹	
P21A	Copolymer	ST/EMA	80/20	28,000	342	1-75	12.7	29.2	1.30 × 10 ⁸	
P22B	Copolymer	ST/EMA	65/35	31,000	320	0-80	10.1	29.7	6.21 × 10 ⁸	
P23A	Copolymer	ST/ODMA	90/10	23,000	355	5-90	10.7	36.4	3.78 × 10 ¹⁰	
P33A	Terpolymer	ST/OMA/DMA	85/7.5/7.5	26,500	329	5-98	15.2	28.7	1.93 × 10 ⁸	
P33B	Terpolymer	ST/OMA/DMA	75/12.5/12.5	28,500	352	1-85	8.1	40.9	2.14 × 10 ¹²	
P33C	Terpolymer	ST/OMA/DMA	85/9/6	5,800	330	5-95	10.4	28.7	1.93 × 10 ⁸	
P33D	Terpolymer	ST/OMA/DMA	85/9/6	5,800	318	5-95	12.2	28.7	1.93 × 10 ⁸	

^a ST: styrene; EMA: ethyl methacrylate; HMA: hexyl methacrylate; OMA: octyl methacrylate; DMA: decyl methacrylate; ODMA: octadecyl methacrylate.
^b Obtained from data at 0.2%-0.5% conversion.

DATA ANALYSIS

Thermal Stability

The thermal stability of a pure inorganic material is regularly determined by the so-called "decomposition temperature," which depends critically on experimental conditions.⁴ This dependence on operational procedure is particularly severe with TG techniques for polymer characterization. Actually, the decomposition temperature obtained from a TG measurement is a poorly defined quantity which does not represent a true decomposition temperature. The new American Society for Testing and Materials (ASTM) Method E537 for measuring thermal stability of chemicals, however, is experimentally a time-consuming process and not applicable to the dynamic TG techniques for measuring polymers.

The thermal stability property adopted in the present investigation is known as Integral Procedural Decomposition Temperature (IPDT).⁵ The data analysis technique was developed primarily for estimating relative thermal stability, from dynamic TG analysis data, of the widely differing behavior of various polymers on a common basis. The calculational methods as described in the cited reference⁵ were incorporated into a FORTRAN program which computed the IPDT value of each TG measurement from the test data of sample weight change versus temperature.

Kinetics

The thermal decomposition kinetics of the TG weight loss data were attributed to the kinetic expression

$$\frac{-d\alpha}{dt} = k_n(1 - \alpha)^n \quad (1)$$

where α is the percent of sample weight fraction reacted at time t and k_n denotes the specific rate with a reaction order n . The reaction rate $-d\alpha/dt$ can be calculated using a differential technique⁶ by directly incorporating the heating rate into the data of temperature versus sample weight fraction.² The specific rate k_n is obtained from the Arrhenius relation

$$k_n = Ae^{-E_a/RT} \quad (2)$$

where T is the absolute temperature, R is the gas constant, and A and E_a are the preexponential factor and activation energy, respectively.

A FORTRAN program was developed to calculate the kinetic parameters E_a and A from a linear least-squares fit of the data in a semilogarithmic form of the combined expression of eqs. (1) and (2). The reaction orders $n = 0, 1/2, 2/3$, and 1 frequently observed in solid-state reactions⁷ were tested in the computations for each set of the TG data.

RESULTS AND DISCUSSIONS

Thermal Stability

The thermal stability expressed in terms of IPDT values as derived from the TG measurements are summarized in the sixth column of Table I. The results indicate that the polystyrene samples all show a comparable thermal stability. In general, the copolymers and terpolymers have similar IPDT values except for P23A and P33B, which are significantly more stable than the other polymers tested. These two samples, of comparable molecular weights, consist of 10% and 25% bulky constituent groups, respectively. It is interesting to note that the composition of ODMA in P23A is approximately half as much as that of the combined OMA and DMA in P33B and that the thermal stability of the copolymer and terpolymer are practically identical even though the size of the pendent group in ODMA is the same as the combined size of those pendent groups in OMA and DMA. This indicates clearly that the size of the side group is at least twice as effective as the amount present in improving the thermal stability of the polymer chains. Similarly, the T_g values of these two polymers have been found to be the same.¹

Kinetic Analysis

Among all the reaction orders attempted, the first-order model is the best fit for the kinetic data of each individual test. Typical first-order plots of the thermal degradation reaction for the polymers are shown in Figures 2–4. The linearity of each plot is generally good for at least two half-lives (seventh column, Table I) of the degradation process. Although some scatter in the early portion and at the end of the reaction were detected in a couple of the polymer samples, such deviations can be attributed to the difficulties for accurate measurements at the beginning and end of an experiment as frequently encountered in kinetic measurements.

The kinetic parameters as derived from the linear plots of Figures 2–4 are summarized in the last two columns of Table I. It is clear that the atactic polystyrene samples all have identical activation energy of 27 kcal/mole regardless of their difference in molecular weight of 33,000–250,000 g/mole. The as-received polymer and the purified sample, P10B and P10C, respectively, show identical degradation kinetics indicating a high purity of the as-received material. The isotactic polystyrene shows definitely different degradation kinetics and has an activation energy of 37 kcal/mole and a higher preexponential factor A than those of the atactic samples. The derived activation energies obtained from the present analysis are considerably lower than the reported 43.0 kcal/mole,⁸ but compared reasonably well with the literature value 30 kcal/mole.⁹ The average molecular weight of the polystyrene samples investigated in the high- E_a studies⁸ are 330,000 and 470,000 g/mole, approximately 100,000 molecular weight units higher than the highest molecular weight sample of our studies, while that of the lower- E_a investigation⁹ is 102,000 g/mole well within the molecular weight range of our work. The reason for the discrepancy between the activation energy of the present analysis and that in reference 8 is not known except that the av-

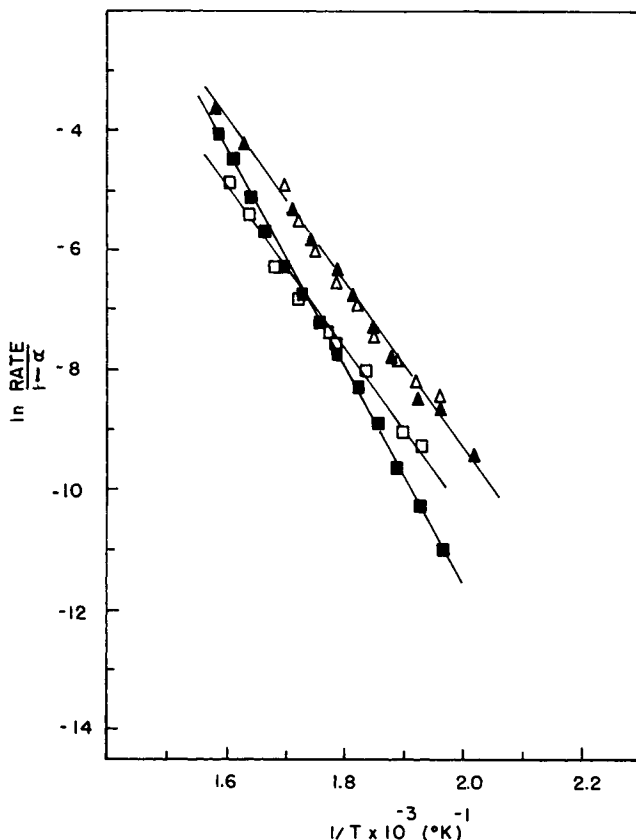


Fig. 2. First-order thermal degradation plots of various polystyrene samples as measured by dynamic thermogravimetric analysis: (Δ) P10B; (\blacktriangle) P10C, (\square) P10D; (\blacksquare) P10E.

erage molecular weight of the samples in the two independent analyses is different. In fact, the measured E_a values differ quite significantly from one author to another⁹ and apparently also depend on the test methods applied.^{9,10}

As indicated in the results given in Table I, the measured E_a 's of the copolymers and terpolymers are independent of the molecular weights, a result consistent with that observed in the styrene-acrylonitrile copolymers.⁸ Furthermore, the measured thermal degradation kinetics of the copolymers and terpolymers are similar and their E_a 's are almost identical (28 ± 1 kcal/mole) when the substituted alkyl methacrylate pendent groups are small and their contents in the polymer are low. When the group is as large as ODMA (P23A) or OMA plus DMA (P33B), its thermal degradation kinetics varies significantly and the activation energies of the reactions are at least 10 kcal/mole higher than that of the polymers with small pendent groups. The difference in activation energy between P23A and P33B indicates additional hindrance effects by a higher concentration of the bulky constituent groups in P33B. Because samples P21A, P23A, P33A, and P33B all have comparable molecular weights, the differences in the activation energies for the respective degradation processes among these polymers may be attributed primarily to the steric effects and concentrations of the bulky groups in the polymer chains. The results clearly show that the effects of the size of the pendent groups are more subtle than those due to the concentrations of the bulky group or groups in the polymer chains.

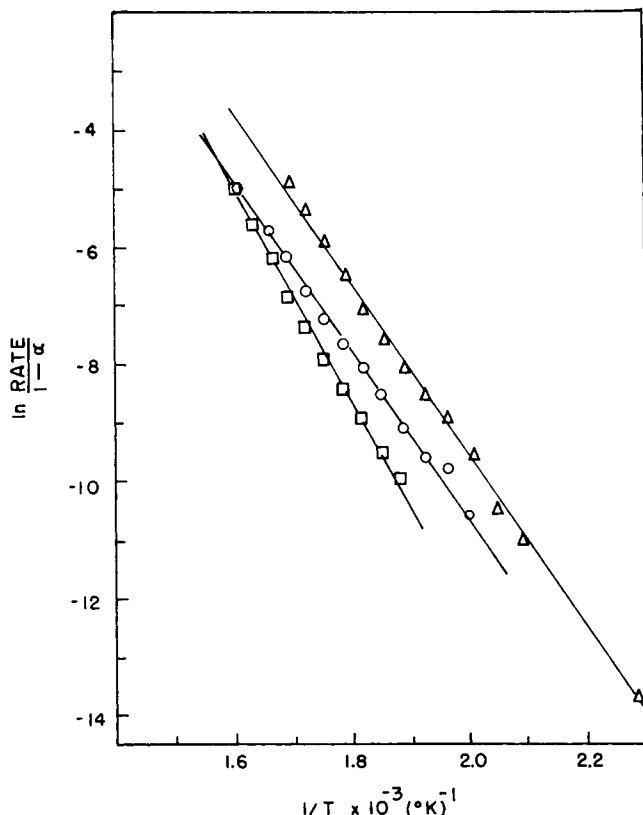


Fig. 3. First-order thermal degradation plots of various styrene-alkyl methacrylate copolymers as measured by dynamic thermogravimetric analysis: (O) P21A; (Δ) P22B; (\square) P23A.

Reaction Mechanism

Although the detailed mechanism of polystyrene degradation reaction depends on the nature of the polymer and is still a subject of controversy,⁹ it is apparent that the polymers tested in this investigation all decompose following a common reaction pattern. Because monomer yield in thermal degradation of polystyrene has been measured to be as high as 40% of the total weight loss,¹¹ it is reasonable that the zip length or the kinetic chain length of the degradation reaction is much higher than the initial degree of polymerization of the polymer. Furthermore, the initial rate analysis as summarized in the eighth column of Table I shows that the initial rates of the degradation reactions are relatively insensitive to the molecular weights of the polymers. These results incorporated with the observed first-order kinetics comply to an endgroup initiation mechanism¹² during which the polymer chains depolymerize by an initial scissioning of the C—C bonds at the chain ends. The analysis agrees closely with the suggestion that the thermal degradation of polystyrene starts out as a random initiation process which quickly converts to end initiation due to the production of unsaturated endgroups by elimination of styrene monomer.¹³

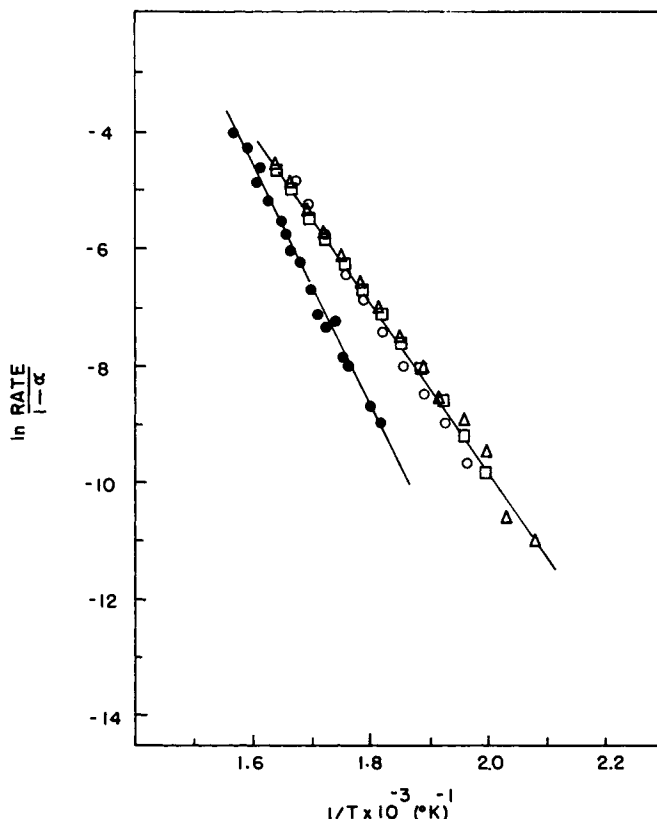


Fig. 4. First-order thermal degradation plots of various styrene-alkyl methacrylate terpolymers as measured by dynamic thermogravimetric analysis: (○) P33A; (●) P33B; (△) P33C; (□) P33D.

CONCLUSIONS

Apparently, the homopolystyrenes and the styrene-alkyl methacrylate copolymers and terpolymers all decompose according to a similar thermal degradation process. The steric effects contributed by small alkyl pendent groups are insignificant. However, as the size of the alkyl side groups increases, the steric effects significantly enhance the chain flexibility (as evidenced in the previous T_g analysis)¹ and thermal resistivity (as shown in TG kinetics) of the polymer and yet without significantly varying the thermal degradation process. Such characteristics for improving flexibility and thermal stability of a polymeric material may be a key point to the search of thermoplastics for effective holographic memory recording applications as discussed previously.^{1,2}

Further investigations into the detailed relationships of glass transition and thermal degradation behavior of polystyrene polymers with the polymer morphologies are being planned. These studies are intended to disclose the mechanisms of steric effects on the characteristic parameters which have not been clarified in the present studies.

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