# INVESTIGATION OF THE DECOMPOSITION OF COPOLYMERS OF STYRENE AND MALEIC ANHYDRIDE USING THERMOGRAVIMETRIC ANALYSIS

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ABSTRACT

The thermal decomposition of several copolymers of styrene (St) or α-methylstyrene (AMS) and maleic anhydride (MAn) were studied by non-isothermal TG in inert atmosphere. From TG data in the temperature range 573–723 K, the kinetic decomposition parameters were calculated using Ozawa's method. The activation energy of decomposition and pre-exponential factor for St/MAn copolymers were: $E_A = 191$–$225$ kJ mol$^{-1}$, log $A = 19.65$–$22.56$ min$^{-1}$ and for an AMS/MAn copolymer $E_A = 266$ kJ mol$^{-1}$, log $A = 26.84$ min$^{-1}$, with a random degradation as the best-fitted mechanism for both types of copolymers. The relation between experimental results and structural characteristics of the copolymers is discussed.

INTRODUCTION

The synthesis, structure, reactivity and applications of copolymers of styrene (St) and maleic anhydride (MAn) have been intensively investigated [1,2]. They are used either in the anhydride form as thermostable thermoplastic polymers, e.g. in polymer blends, or in chemically-modified forms as dispersing agents, emulsifiers, auxiliary agents in the paper and textile industry, in adhesives, coatings, etc.

The relatively high values of $T_g$, softening point and decomposition temperature of alternating St/MAn copolymers, poly [styrene-alt-(maleic anhydride)], are a consequence of the alternating arrangement of cyclic, polar anhydride units and nonpolar, substituted vinylaromatic units in the main chain. The thermal properties of such copolymers have been investigated by several authors [3–5]. Urushizaki et al. [3] studied thermal decomposition of St/MAn copolymers in the temperature range 475–593 K. According to their results, decomposition begins above 473 K with the main volatile products isolated in the range 553–573 K being water, $CO_2$, toluene, styrene, ethylbenzene, 1,3-diphenylpropane, 3-phenyl-2-cyclohexenone and γ-phenylbutyric acid, with 80 wt.% residue. Rätzsch and Phien Vo [4] compared thermal properties of the anhydride and imide form of St/MAn

copolymers. Kutynina et al. [5] studied the influence of different chemical forms of ST/MAn copolymers (anhydride, acid, salt) on their thermal properties up to 573 K.

In this work the thermal decomposition kinetic parameters of a series of St/MAn copolymers were calculated from thermogravimetric data in the temperature range 573–723 K using an approximate integral Ozawa method [6,7], and correlated with some structural characteristic of the copolymers.


EXPERIMENTAL


Monomers and solvents were purified before use by conventional methods. Maleic anhydride (98 wt.%) was crystallized from benzene. Styrene and α-methylstyrene (AMS) were treated to remove polymerization inhibitor and distilled. Toluene and acetone were dried and distilled in nitrogen. The initiators used were azobisisobutyronitrile (AIBN; 98 wt.%) and t-butylperoxypivalate (Trigonox 25c75; 75 wt.%), both from Akzo. Thioglycolic acid (TGA; 98 wt.%) from Aldrich was used as the molecular weight modifier.

Copolymers were prepared in solution (toluene or acetone) from equimolar quantities of MAn and St or AMS in the presence of initiator. In the preparation of St/MAn 1 the modifier, TGA, was used. Variations in the composition of the reactants and in the reaction conditions used in preparation of individual copolymers are described in Table 4. Copolymerization of St/MAn 1 was performed in ampoules without stirring, while the other samples (St/MAn, 2, St/MAn 3, AMS/MAn) were prepared in well stirred reaction systems (200 rpm). Samples St/MAn 1600 and St/MAn 350 were purchased from Aldrich and had declared number average molecular weights of 1600 and 350 000, respectively.

All samples were precipitated from acetone solution with a benzene/petrol ether mixture and dried in vacuum and 353 K to constant weight. The content of MAn in copolymers was determined by potentiometric titration. The limiting viscosity numbers, $[\eta]$, were determined at 25°C in tetrahydrofuran using a Ostwald–Fenske dilution viscometer. The average molecular weights were calculated from $[\eta]$ values using the Chow equation [8] $[\eta] = 3.98 \times 10^4 \, M_w^{0.596}$

Thermogravimetric analysis of finely-powdered samples were performed on a Perkin–Elmer TGS-2, with a nitrogen flow rate 8 ml min$^{-1}$, in the temperature range 338–873 K and with three different heating rates, 5, 10 and 20 K min$^{-1}$. The average sample size was 4 mg. Before TG analysis all the samples were quickly preheated to 423 K.

Differential scanning calorimetry (DSC) was done using a Perkin–Elmer Model DSC-2 at a scanning rate of 20 K min$^{-1}$.

RESULTS

TG and DTG curves of four separate samples are shown in Fig. 1. Kinetic decomposition parameters of all samples, in the range 573–723 K, were calculated by Ozawa's method [6,7]. Only one form of the final equation (1) is given here in order to define terms used in the calculation procedure.

$$\log \text{hr} = \log(AE_A/\text{hr } R) - 2.314 - 0.4567(E_A/RT) - \log g(c) \qquad (1)$$

where

$$g(c) = (AE_A/\text{hr } R)p(x); \qquad \text{with } x = E_A/RT$$

where hr is the heating rate (K min$^{-1}$); $A$ is the pre-exponential factor of the Arrhenius equation (min$^{-1}$); $E_A$ is activation energy (kJ mol$^{-1}$); $R$ is the gas constant (8.314 J mol$^{-1}$); $g(c)$ is the conversion function and $T$ is absolute temperature (K). The fractional conversion $(1 - c)$ is defined as the residual weight of the sample at a specified temperature divided by the total weight of the sample decomposed within the temperature range examined.

The calculation procedure of TG data is illustrated on sample St/MAn 2. Integral TG curves for three different heating rates were obtained by plotting the fractional conversion values, $(1 - c)$ against the reciprocal temperature $1/T$ (Fig. 2). By plotting the logarithm of the heating rate against $1/T$ for each indicated fractional conversion (the values of hr, $1/T$
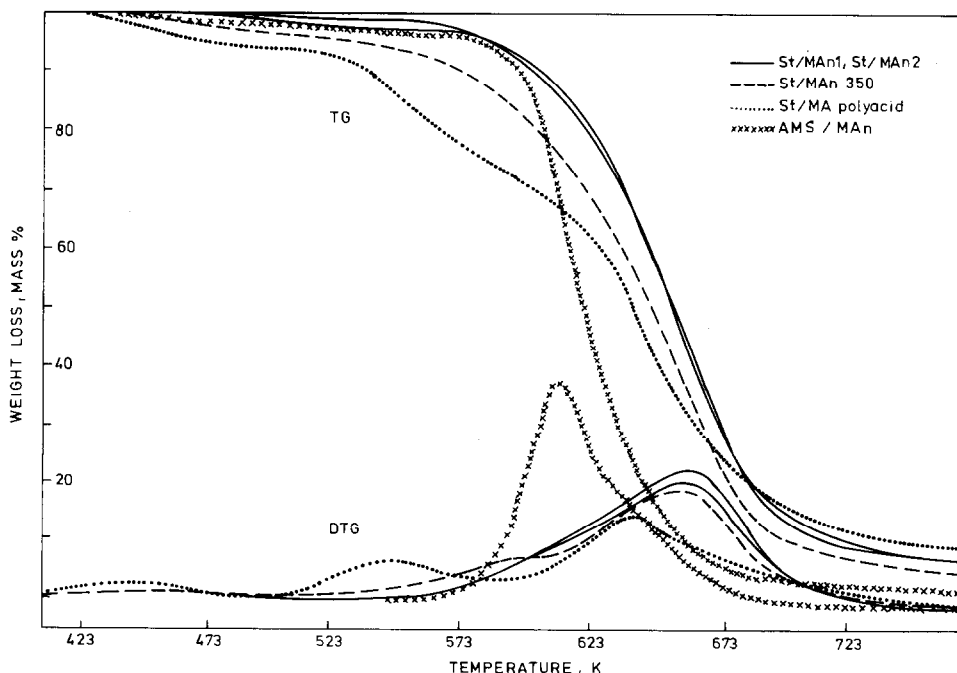


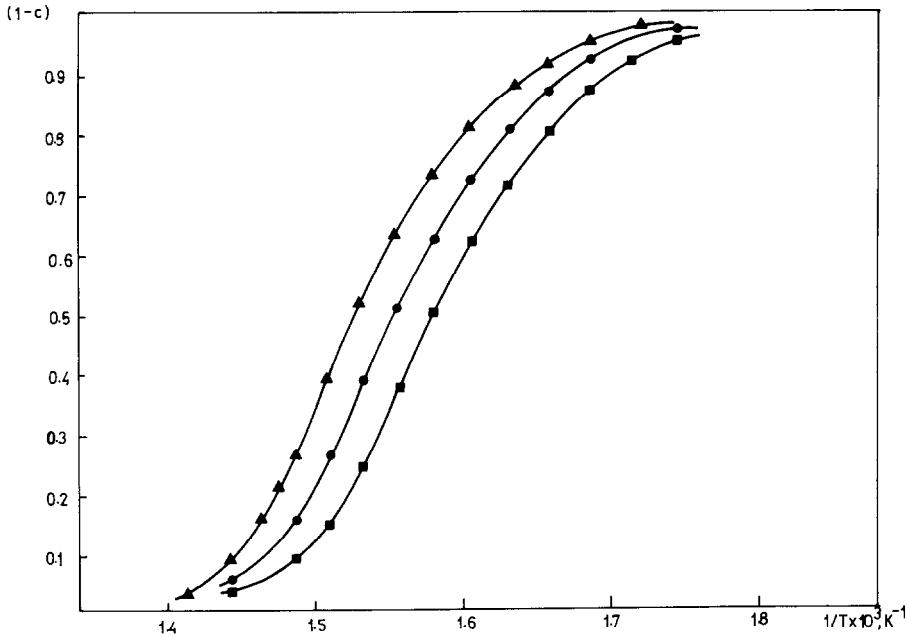Fig. 1. Primary TG and DTG curves of St/MAn, AMS/MAn and St/MA copolymers.

Fig. 2. Thermogravimetric curves of St/MAn 2 copolymer plotted as the fractional conversion, $(1 - c)$, against the reciprocal absolute temperature, $1/T$. Heating rates: ▲, 5 K min$^{-1}$; ●, 10 K min$^{-1}$; ■, 20 K min$^{-1}$.

and $(1 - c)$ are taken from the TG curves in Fig. 2), a series of parallel isoconversional straight lines was obtained (Fig. 3). From the slopes of these lines $E_A$ values were calculated using eqn. (2) and least squares fitting

$$\text{slope} = \frac{\log hr}{1/T} = 0.4567 \frac{E_A}{R} \tag{2}$$

The approximate constancy of $E_A$ with conversion is shown in Table 1. The average value of the activation energy of decomposition of St/MAn 2 is $217 \pm 6$ kJ mol$^{-1}$.

TABLE 1

Activation energy of decomposition of St/MAn 2 copolymer at various conversions

| $(1 - c)$ | $E$ (kJ mol$^{-1}$) | $(1 - c)$ | $E$ (kJ mol$^{-1}$) |
|---|---|---|---|
| 0.20 | 228.09 | 0.55 | 223.59 |
| 0.25 | 227.21 | 0.60 | 216.25 |
| 0.30 | 216.25 | 0.65 | 210.73 |
| 0.35 | 218.12 | 0.70 | 198.95 |
| 0.40 | 219.00 | 0.75 | 203.00 |
| 0.45 | 228.34 | 0.80 | 206.63 |
| 0.50 | 228.34 | | |

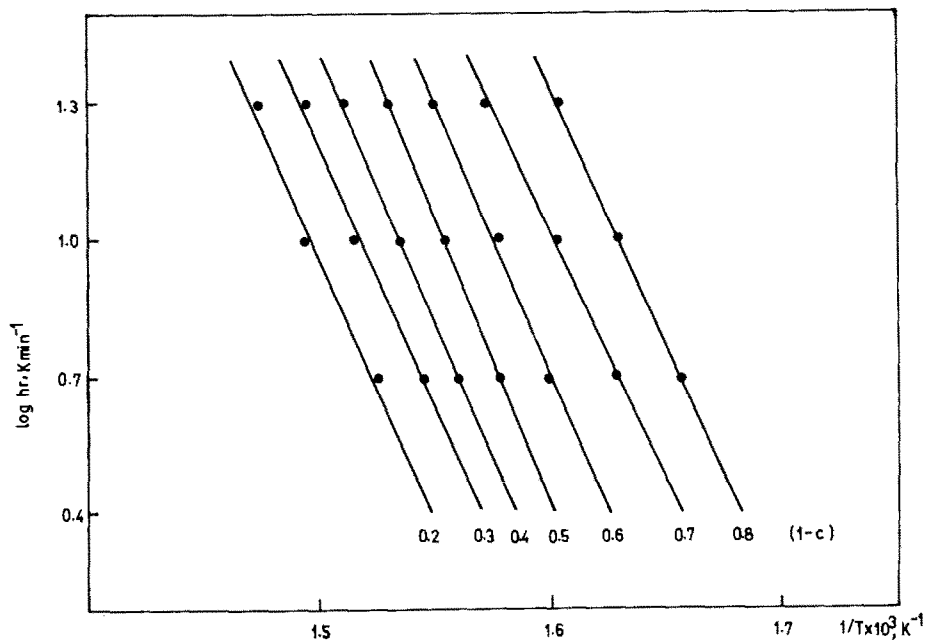Average value of activation energy: $E_A = 217.27 \pm 6.0$ kJ mol$^{-1}$

Fig. 3. Plot of logarithm of heating rate, log hr, vs. the reciprocal absolute temperature, $1/T$, for indicated fractional conversions, $(1-c)$, in decomposition of St/MAn 2 copolymer.

TABLE 2

Calculation of pre-exponential factor, log $A$, in thermal decomposition of St/MAn 2 copolymer. Comparison of the experimental values of conversion $(1-c)$ and the conversion values calculated from the estimated kinetic parameters

| $(1-c)$ exptl. | $1/T \times 10^3$ | log $p(E/RT)$ | $\dfrac{\log(E/\text{hr } R)}{p(E/RT)}$ | $dx/g(x)$ | log $A$ | $(1-c)$ calc. |
|---|---|---|---|---|---|---|
| 0.20 | 1.492 | −19.897 | −19.486 | 2.303 | 21.79 | 0.25 |
| 0.25 | 1.502 | −20.015 | −19.603 | 2.040 | 21.64 | 0.28 |
| 0.30 | 1.512 | −20.133 | −19.721 | 1.833 | 21.55 | 0.31 |
| 0.35 | 1.522 | −20.251 | −19.839 | 1.661 | 21.50 | 0.34 |
| 0.40 | 1.530 | −20.345 | −19.934 | 1.470 | 21.40 | 0.37 |
| 0.45 | 1.540 | −20.463 | −20.051 | 1.347 | 21.40 | 0.43 |
| 0.50 | 1.550 | −20.581 | −20.169 | 1.237 | 21.41 | 0.45 |
| 0.55 | 1.560 | −20.699 | −20.287 | 1.109 | 21.40 | 0.51 |
| 0.60 | 1.570 | −20.817 | −20.405 | 0.994 | 21.40 | 0.56 |
| 0.65 | 1.582 | −20.958 | −20.546 | 0.892 | 21.44 | 0.61 |
| 0.70 | 1.596 | −21.123 | −20.711 | 0.799 | 21.51 | 0.70 |
| 0.75 | 1.608 | −21.264 | −20.853 | 0.693 | 21.55 | 0.77 |
| 0.80 | 1.625 | −21.465 | −21.053 | 0.598 | 21.65 | 0.86 |

The mean of the pre-exponential factor: log $A = 21.51 \pm 0.03$ min$^{-1}$
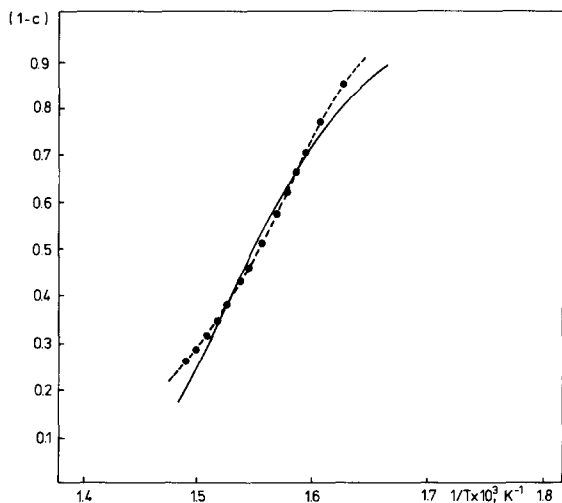
Fig. 4. Comparison of the experimental master TG curve (————) with TG curve (— — —) obtained from the calculated kinetic decomposition parameters of St/MAn 2 copolymer.

The next step in the calculation was determination of the mechanism of decomposition, and the pre-exponential factor. From an experimental master curve (obtained by lateral shifting and superposition of TG curves at three different heating rates, Fig. 2) and the mean value of $E_A$ estimated, the plot of $(1 - c)$ against $\log[(E_A/hr\ R)p(E_A/RT]$ was obtained and superimposed to fit one of Ozawa's theoretical TG curves [6]. The best fit was achieved with the theoretical curve for random degradation $L = 2$ ($L$ is the least number of repeating units of non-volatilized polymer). The length of abscissa shift corresponds to an approximate $\log A$ value. A more precise value of $\log A$ was obtained by the subtraction of $\log[(E_A/hr\ R)p(E_A/RT)]$

TABLE 3

Kinetic parameters of thermal decomposition of St/MAn, AMS/MAn and St/MA copolymers calculated from TG using Ozawa's method (random degradation $L = 2$ mechanism in all cases)

| Copolymer | $E_A$ (kJ mol$^{-1}$) | $\log A$ (min$^{-1}$) | $T_M$ [a] (K) |
|---|---|---|---|
| St/MAn 1600 | 191.11 ± 6.65 | 19.65 ± 0.05 | 648 |
| St/MAn 1 | 190.00 ± 2.18 | 19.89 ± 0.03 | 653 |
| St/MAn 2 | 217.27 ± 6.01 | 21.51 ± 0.03 | 653 |
| St/MAn 3 | 210.27 ± 5.92 | 21.26 ± 0.04 | 653 |
| St/MAn 350 | 224.85 ± 5.58 | 22.56 ± 0.06 | 653 |
| St/MA polyacid | 271.31 ± 23 | 26.70 ± 0.03 | 633 |
| AMS/MAn | 266.00 ± 11.29 | 26.84 ± 0.00 | 609 |

[a] $T_M$, Temperature corresponding to the maximum rate of mass loss (from DTG curve with heating rate 10 K min$^{-1}$).

from the $\int dx/g(x)$ values of random degradation with $L = 2$ for each 0.05 change in $(1 - c)$ (see Table 2, columns 4, 5 and 6). The mean value of log $A$ is $21.51 \pm 0.12$ min$^{-1}$.

Relatively good agreement between the experimental master curve and the TG curve calculated from the estimated $E_A$ and log $A$ values for sample St/MAn 2 is shown in Fig. 4. Kinetic decomposition parameters of other samples were calculated using the same procedure. The results are shown in Table 3, which includes the temperatures of maximum decomposition rate, $T_M$ derived from DTG curves obtained at a heating rate of 10 K min$^{-1}$.

DISCUSSION

The differences in the copolymers studied, i.e. the preparation conditions, composition, limiting viscosity number, molecular weights and $T_g$ are presented in Table 4. The content of MAn in individual copolymers and the relatively high $T_g$ values suggest an equimolar relation between MAn and St or AMS and an alternating arrangement of monomer units within the polymer chains.

The TG analysis of all copolymers was performed under the same conditions. The shapes of the TG–DTG curves (Fig. 1) in the temperature range 573–723 K correspond to a single-step process. The residues at 723 K were 5–10 wt.%. A chain scission is probably the main decomposition reaction for St/MAn copolymers in the actual range of our calculations (fractional conversion 0.2–0.8; temperature 600–660 K). The mechanism of random degradation with $L = 2$ provides the best fit in the comparison of the experimental data with Ozawa's theoretical TG-curves [6] (Table 3).

The spread of $E_A$ ($191 - 225$ kJ mol$^{-1}$) and log $A$ ($16.65 - 22.56$ min$^{-1}$) values for copolymers of the same composition (Table 3) is possibly a consequence of structural heterogeneities of the polymer and variations in molecular weights. The lowest limiting value of $E_A$ is for copolymer St/MAn 1600 with the lowest $M_w$, $T_g$ and $T_M$ values. It is in agreement with recently estimated correlations between $M_w$ and $E_A$ for low molecular weight polystyrenes [9]. The presence of partially hydrolysed anhydride groups (detected as carbonyl vibrations at 1720 cm$^{-1}$ in IR) causes an earlier mass loss [10] (at 433–453 K), lower $T_g$ values, more complex degradation, slower rate and higher energy of decomposition. This is illustrated by the shapes of TG–DTG curves (Fig. 1) and by the values of kinetic parameters (Table 3) of partially hydrolysed St/MAn 350 copolymer and 'pure' St/MA polyacid. The average decomposition rates in the temperature range examined are also different: 0.97–1.00 wt.% K$^{-1}$ for the first four St/MAn samples in Table 3; 0.78 wt.% K$^{-1}$ for partially hydrolysed St/MAn 350 and 0.61 wt.% K$^{-1}$ for St/MA polyacid.

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TABLE 4

Copolymerization conditions and some characteristics of St/MAn, AMS/MAn and St/MA copolymers

| Copolymer | Copolymerization conditions | Content of MAn (wt.%) | $[\eta]$ (dl g$^{-1}$) | $M_w$ | $T_g$ (K) |
|---|---|---|---|---|---|
| St/MAn 1600 | Precipitated low molecular weight commercial St/MAn copolymer | 45.8 | 0.088 | 8600 | 456 |
| St/MAn 1 | 20 wt.% of equimolar mixture of St and MAn in toluene, 1% AIBN, 1% TGA, 348 K, 5 h. | 48.4 | 0.189 | 31000 | 479 |
| St/MAn 2 | 10 wt.% of equimolar mixture of St and MAn in toluene, 0.5% AIBN. Gradual addition of St to stirred solution of MAn and AIBN, 348 K, 6 h. | 48.2 | 0.269 | 56000 | 485 |
| St/MAn 3 | Simultaneous stirring of 10 wt.% of equimolar mixture of St and MAn in toluene, 0.5% AIBN, 353 K, 4 h. | 47.8 | 0.350 | 92000 | 484 |
| St/MAn 350 | Precipitated high molecular weight commercial St/MAn copolymer | 46.5 | 0.968 | 480510 | 450 |
| St/MA polyacid | Poly[styrene-alt-(maleic acid)], hydrolyzed St/MAn copolymer | 47.2 | 0.336 | 81400 | 458 |
| AMS/MAn | Stirred solution of 20 wt.% equimolar mixture of AMS and MAn in acetone, 3% Trigonox 25c75, 333 K, 6 h. | 41.2 | 0.139 | 18500 | 488 |

The TG curve of AMS/MAn copolymer has the steepest slope (Fig. 1), the highest $E_A$ (Table 3) and the highest average rate of decomposition 1.375 wt.% $K^{-1}$, because the steric hindrance of $\alpha$-methyl groups in AMS makes depolymerization easier.

REFERENCES

1  M. Rätzsch, Progr. Polym. Sci., 13 (1988) 277.
2  S.R. Ebdon and C.R. Towns, J. Macromol. Sci. Rev., Macromol. Chem. Phys., C26 (1986) 523.
3  M. Urushizaki, S. Matski, S. Sakamoto and H. Aida, Kobunshi Robunshu, 32 (6) (1975) 342.
4  M. Rätzsch and Phien Vo, Faserforsch. Textiltech., 27 (1976) 357.
5  I.G. Kutyanina and N.K. Baramboim, Izv. Vyssh. Uchebn. Zaved. Tekhnol. Prom., 25 (1) (1982) 31.
6  T. Ozawa, Bull. Chem. Soc. Jpn. 38 (1965) 1881.
7  T. Ozawa, J. Therm. Anal., 7 (1975) 601.
8  C.D. Chow,, J. Appl. Polym. Sci., 20 (1976) 1619.
9  M. Heitz, F. Carrasco, R.P. Overend and E. Chornet, Thermochim. Acta, 142 (1989) 83.
10 M. Rätzsch, V. Steinert, J. Rochner and M. Arnold, Plaste Kautsch., 31 (5) (1984) 165.