THERMAL DEGRADATION MECHANISM OF METHACRYLONITRILE-STYRENE COPOLYMERS ON FLASH PYROLYSIS

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Abstract

The thermal degradation mechanisms of random copolymers of methacrylonitrile (MAN) and styrene (St) have been investigated by pyrolysis gas chromatography in the temperature range of 358 to 920°C using a Curie point pyrolyzer (JHP-2) and comparing results with the results from TG/DTA-FTIR apparatus (SII-6200, JASCO-320). The amount of St monomer from decomposition of the copolymer is higher than that from P(St) alone; whilst that of MAN monomer from copolymer is lower than that from P(MAN). This phenomenon reflects the boundary effect in the pyrolysis of copolymer. The thermal degradation mechanisms of copolymers are discussed in terms of the competition between the depolymerization and the back biting reaction on the basis of bond dissociation energies of C–C and C–H bonds in the copolymer chain.

Keywords: Curie-point pyrolyzer, poly(methacrylonitrile-co-styrene), pyrolysis-gas chromatography

Introduction

Investigation of the thermal degradation of macromolecules by pyrolysis gas chromatography (Py-GC) is an important field of polymer science, for studying the evolved gases and thermal stability of fibers, plastics and rubbers. In general, the yields of monomer molecules regenerated from pyrolysis of copolymers differ from those of the corresponding homopolymers. This phenomenon can be ascribed to the difference of thermal degradation mechanism at the boundaries of comonomers formed due to the 'blockiness' in the copolymer chain.

One of the authors has defined previously a 'boundary effect' in the thermal degradation of copolymers and has utilized this effect in the measurement of sequence distribution in the random copolymers [1]. For the sequence -A-A-A· · ·A-B-A-A-, the regeneration probability P_{AA} of monomer A in sequence A is different from that of monomer A which is bounded on sequence B, P_{AB}. Similarly for monomer B.

$$\cdot AA\sim\sim\sim \rightarrow A +\cdot A \sim\sim\sim \qquad P_{AA}$$

$$\cdot AB \sim\sim\sim \rightarrow A +\cdot B \sim\sim\sim \qquad P_{AB}$$
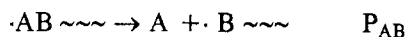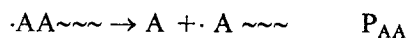
A boundary effect parameter β_A can be defined by Eq. (1),

$$\beta_A = P_{AB}/P_{AA} \tag{1}$$

On the other hand, the run number R, defined by Harwood [2], is the average number of monomer sequences (runs) occurring in a copolymer per 100 monomer units. The run fraction R_f can be calculated easily by Eq. (2),

$$R_f = R/100 = 2x/(r_A x^2 + 2x + r_B) \tag{2}$$

where r_A and r_B are monomer reactivity ratios for A and B monomers, respectively; and x is the molar ratio of monomers, A/B, in the feed.

The number fractions of A–B and A–A linkages are calculated as follows:

number fraction of A–B linkages $= R_f/2$
number fraction of A–A linkages $= \Phi_A - R_f/2$
where Φ_A is the mol fraction of unit A in the copolymer.

The yield of unit A regenerated from copolymer: $Y(A)_{co}$ is given by Eq. (3).

$$Y(A)_{co} = \frac{1}{\Phi_A}\left\{\left[\Phi_A - \frac{R_f}{2}\right]P_{AA} + \frac{R_f}{2}P_{AB}\right\} \tag{3}$$

The probability P_{AA} is equal to the yield of A from the homopolymer of A.

The boundary parameter β values of monomer A and B can be computed by Eqs (4) and (5).

$$\beta_A = 1 - \Phi_A\left(1 - \frac{Y(A)_{co}}{Y(A)_{ho}}\right)\left(\frac{r_A x^2 + 2x + r_B}{x}\right) \tag{4}$$

$$\beta_B = 1 - \Phi_B\left(1 - \frac{Y(B)_{co}}{Y(B)_{ho}}\right)\left(\frac{r_A x^2 + 2x + r_B}{x}\right) \tag{5}$$

The boundary effect depends not only on the kind of terminal monomer unit, but also depends on the pyrolysis apparatus, pyrolysis temperature, mass of sample and other factors.

In this study, the thermal degradation mechanisms of random copolymers of methacrylonitrile(MAN) and styrene(St) have been investigated by Py-GC using a Curie-point pyrolyzer. Results are compared with the results from TG/DTA-FTIR. Furthermore, the difference of monomer yielded from the copolymers and the corresponding homopolymers has been discussed in connection with the difference of C–C bond dissociation energies in the depolymerization reaction and also that of C–H bond dissociation energies for hydrogen abstraction in the back biting reaction by a terminal radical, which competes with depolymerization.

Experimental

Materials

Distilled St and MAN monomers purchased from Wako Junyaku Kougyo were used. PSt, PMAN and five copolymers of different compositions (C–1 to C–5)

were synthesized by radical polymerization initiated by 1.0 mol% of azobisisobuty-ronitrile(AIBN). PSt, PMAN, C–1 (F_{MAN}, molar fraction of copolymer, is 0.67) and C–2 (F_{MAN}=0.33) were obtained by bulk polymerization at 60°C in nitrogen atmosphere. The other three copolymer samples, C–3 (F_{MAN}=0.78), C–4 (F_{MAN}=0.71) and C–5 (F_{MAN}=0.55), were polymerized in sealed tubes after degassing 4 to 5 times using a repeated freeze and melt method. Polymerization times were controlled so that conversions could be around 5 to 10%. Copolymer compositions were calculated by Mayo-Lewis-Sakurada's equation using monomer reactivity ratios: r_{St}=0.39, r_{MAN}=0.32, at 60°C; r_{St}=0.37, r_{MAN}=0.41, at 80°C [3] and confirmed using relative intensities of characteristic bonds in the IR spectra.

Procedures

TG/DTA-FTIR: A TG/DTA-FTIR real-time measuring device (SII-6200, JASCO-320) was used.

Pyrolysis-gas chromatography: Polymer samples were pyrolyzed by a Curie Point Pyrolyzer (JHP-2). The ferromagnetic foils were coated with a polymer sample using a dilute THF solution. After removal of solvent, the foils coated by 0.1 to 0.3 µg of polymer samples were heated by a high frequency electromagnetic field for 3 s in a quartz pipe. The pyrolysis products were swept into the column of the GC (HP5890) by helium gas and were analyzed.

For quantitative analysis of monomers in the pyrolysis products by GC, absolute calibration curves were used.

Results and discussion

From the results of TG/FTIR measurements at 10 to 20°C min^{-1} heating rates, it was found that poly(MAN-co-St) (molar ratio 1:1) was degraded in one step in the
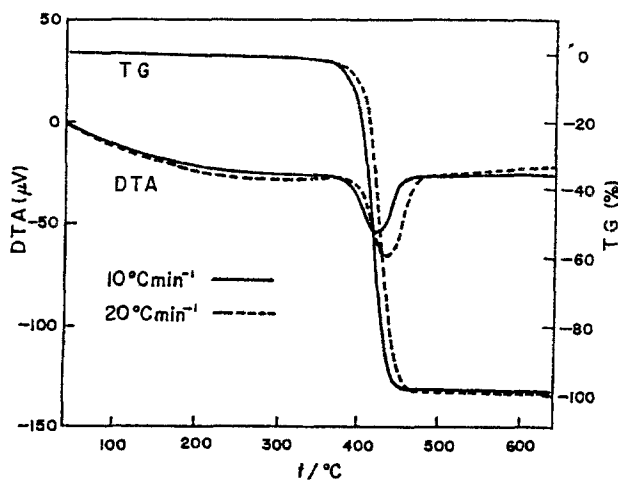

Fig. 1 TG and DTA curves for the poly(MAN-co-St) (F_{MAN}=0.55): heating rates 10 and 20°C min^{-1}, flow rate of nitrogen 100 ml min^{-1}

temperature range of 370 to 450°C as shown in Fig. 1. On continuous heating at relatively high temperature, PMAN can undergo nearly quantitative depolymerization to monomers under some conditions [4]. In the thermal degradation of PSt, 60 to 70% of monomer molecules were regenerated and some dimers and trimers were produced. The copolymer of MAN and St should preferentially depolymerize similarly to PMAN. On the contrary, in the rapid pyrolysis of polymers using the Curie-point pyrolyzer, the yields of regenerated monomers were not as high. As shown in Fig. 2, below 300°C the depolymerization of PMAN hardly occurred, whereas the yield of MAN monomer increased rapidly over the temperature range of 350 to 500°C and reached 75%. The yield of MAN monomer from poly(MAN-co-St) reached only to 55% at 500°C. The yield of monomer from PSt increased steeply to reach 50% when the temperature was raised from 450 to 500°C. The yield of styrene and methacrylonitrile monomers from the copolymers increased almost to 75% at 500°C. Regardless of the composition of the copolymers, the yield of MAN monomer decreased as the St unit content in the copolymer increased, while the yield of St monomer increased with the MAN unit content in the copolymer. This phenomenon may be due to the boundary effect in the pyrolysis of the copolymer.

The average boundary effect β values of the copolymers of MAN and St with different composition at various temperatures were calculated according to Eqs (4) and (5). The β values changed exponentially with temperature.
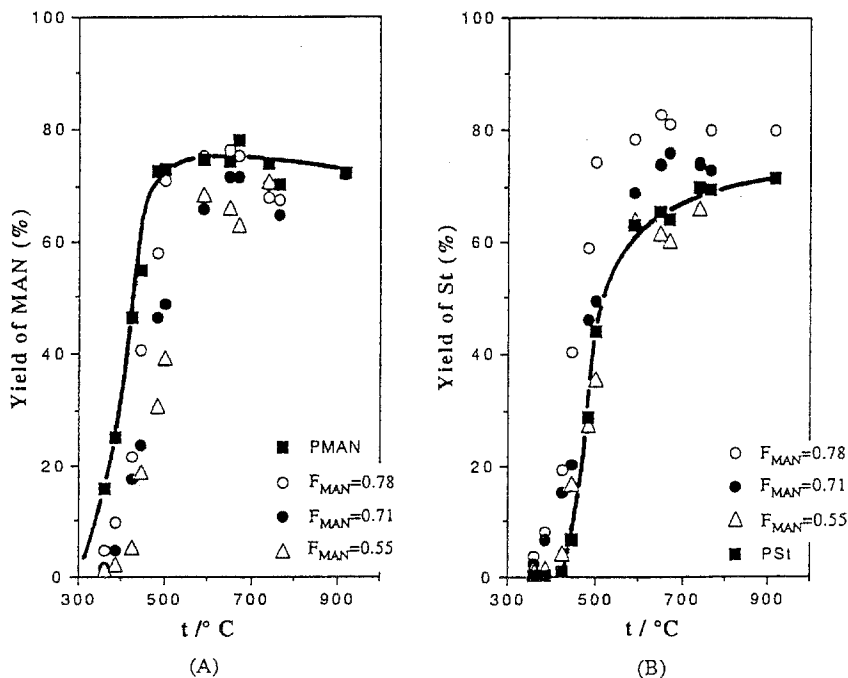

Fig. 2 Effect of temperature and copolymer composition on the yields of monomers from the copolymers of MAN and St and the corresponding homopolymers: (A) MAN monomers, (B) St monomers
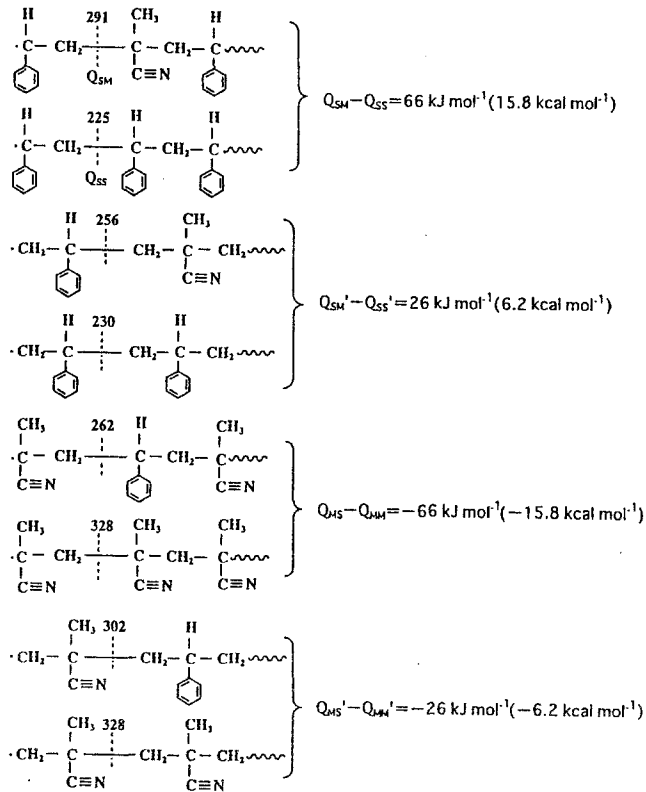
The β value for St decreased steeply from 10 at 423°C and the β value for MAN increased from zero at the same time. Both values tended to be unity at temperatures higher than 600°C. To investigate the sequence distribution of this copolymer, the appropriate temperature range of flash pyrolysis was between 500 and 600°C.

The change in the regeneration probabilities of monomers from the copolymer is thought to be related to the C–C bond dissociation energy in the polymer chain. Here the C–C bond dissociation energy, Q_{C-C}, is estimated using Vedeneev's method [1, 5], which is shown as follows:

$$Q_{C-C} = E'_{C-C} - (B_R + B_X) =$$

$$= E'_{C-C} - \left(\sum_m M_i \alpha_i \exp\{-\omega m\} + aE_{conj} \right) - \left(\sum_n N_i \alpha_i \exp\{-\omega n\} + bE_{conj} \right)$$

After deducting the stabilization energies of radicals due to atomic groups R and X, B_R and B_X respectively, from the characteristic energy E'_{C-C} of the C–C bond, the bond dissociation energy for a particular C–C bond is calculated. Where M_i and N_i are the numbers of bonds of type i which are bonded with the mth and nth carbons from the bond under consideration, where α_i is the specific value of the stabilization

$Q_{SM} - Q_{SS} = 66$ kJ mol^{-1} (15.8 kcal mol^{-1})

$Q_{SM}' - Q_{SS}' = 26$ kJ mol^{-1} (6.2 kcal mol^{-1})

$Q_{MS} - Q_{MM} = -66$ kJ mol^{-1} (−15.8 kcal mol^{-1})

$Q_{MS}' - Q_{MM}' = -26$ kJ mol^{-1} (−6.2 kcal mol^{-1})
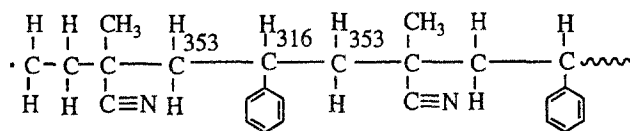
Scheme 1

due to a given bond type, and where $\exp\{-\omega\}$ is a coefficient having the value 0.4. In this relationship, a and b are the numbers of conjugated groups adjacent to the bond under consideration and E_{conj} is the stabilization energy imparted to a free radical by a conjugated group. In this study, the following values of the constants in Vedeneev's equation were used: $E'_{C-C}=599.6$ J mol^{-1}, $E'_{C-H}=534.7$ J mol^{-1}, $\alpha_{C-H}=41.8$ J mol^{-1}, $B_{-C_6H_5}=108.8$ J mol^{-1}, $B_{-C\equiv N}=34.7$ J mol^{-1}, $E_{conj}=81.2$ J mol-1, $\exp\{-\omega\}=0.4$. As shown in Scheme 1, the difference in bond dissociation energies for cutting off each monomer molecule will be in the range of 26 to 66 kJ mol^{-1}. When the MAN monomer unit, which is easier to generate as monomer, is linked with the same unit, the bond dissociation energy calculated by Vedeneev's equation increased. But, in fact, the yields of monomers increased with the content of MAN. This result is inconsistent with the idea previously presented by one of the authors [1], that the higher the bond dissociation energy is, the lower the yield of monomer is. Consequently, in this study we reconsidered the thermal degradation mechanism of copolymers adopting the back biting mechanism.
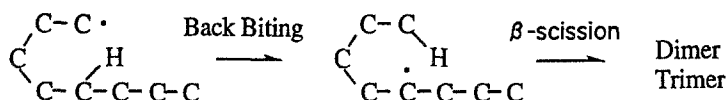
As shown above, the hydrogen atom is abstracted by a terminal radical via 6-membered ring formation, and this is the so-called back biting mechanism. Then, β-scission occurred successively, so as to regenerate dimers and trimers. The C–H bond dissociation energies were also calculated according to Vedeneev's method using the equation shown below:

$$Q_{C-H} = E'_{C-H} - (B_R + B_X) =$$

$$= E'_{C-H} - \left(\sum_m M_i\alpha_i \exp\{-\omega m\} + aE_{conj}\right) - \left(\sum_n N_i\alpha_i \exp\{-\omega n\} + bE_{conj}\right)$$
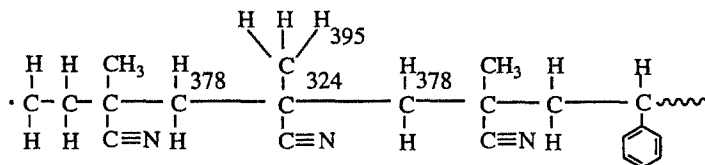
The figures shown in the above scheme are the C–C bond and the C–H bond dissociation energies in kJ mol^{-1}. The C–H bond dissociation energy of the α-position of the St unit is 316 kJ mol^{-1}, while the energy of the C–H bond in the methyl group of MAN is 395 kJ mol^{-1}. Then, it can be considered that, if a 'pen-penultimate' unit is MAN, the abstraction of H atom by a terminal radical from the methyl group of

MAN is more difficult than that from the α position of St. The probability of H atom abstraction by back biting will decrease with the increasing of MAN unit content. Therefore, we consider that for copolymers containing MAN units depolymerization occurs preferentially and that the yield of monomer becomes larger. A detailed discussion on this point will be given elsewhere.

Concluding remarks

Poly(MAN-co-St) generates monomers and dimers on pyrolysis, independent of whether it is continuously heated with constant heating rate or rapidly heated by a flash pyrolysis. The yield of styrene monomer from the copolymer increases, whilst the yield of methacrylonitrile decreases. This reflects the boundary effect in the pyrolysis of the copolymer. Estimating the dissociation energy of the C–C bond by Vedeneev's method, the dissociation energy for the MAN unit is higher than that for the St unit, but it is inconsistent with the experimental result. It is necessary to analyze the thermal degradation mechanism of the copolymer by considering the competition between the back biting process and the depolymerization.

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