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Z. Janović[a]; Lj. Tomašek[a]; T. Malavašič[b]
[a] Faculty of Chemical Engineering and Technology University of Zagreb, Zagreb, Croatia [b] National Chemical Institute, Ljubljana, Slovenia

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COPOLYMERIZATION AND COPOLYMERS OF 2,4,5-TRIBROMOSTYRENE WITH STYRENE AND ACRYLONITRILE

Z. JANOVIĆ* and LJ. TOMAŠEK

Faculty of Chemical Engineering and Technology
University of Zagreb
Zagreb, Croatia

T. MALAVAŠIČ

National Chemical Institute
Ljubljana, Slovenia

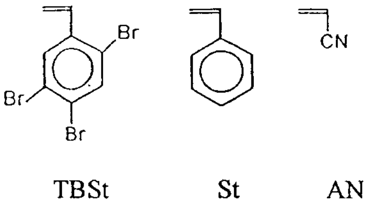
ABSTRACT

2,4,5-Tribromostyrene (TBSt) was copolymerized with styrene (St) or acrylonitrile (AN) in toluene solution using 2,2′-azobisisobutyronitrile as free radical initiator. The copolymerization reactivity ratios were found to be for the system TBSt/St $r_1 = 1.035 \pm 0.164$ (TBSt) and $r_2 = 0.150 \pm 0.057$ (St), and for the system TBSt/AN $r_1 = 2.445 \pm 0.270$ (TBSt) and $r_2 = 0.133 \pm 0.054$ (AN). The *e* and *Q* values were also calculated. The initial copolymerization rate, R_p, for both systems linearly increases as the content of TBSt in the monomer mixture increases. However, these values are somewhat higher when AN was used as a comonomer. A similar behavior has also been established for the course of the copolymerization reactions to high conversion. The resulting copolymers and TBSt-homopolymer show similar thermal stabilities of polystyrene. However, the glass transition temperature increases markedly with increasing TBSt content.

INTRODUCTION

Free-radical homopolymerization and copolymerization of halogen-substituted styrene monomers have been described in several papers [1–4]. It was shown than an increase in styrene halogenation results in an increase in the rate of polymerization and in the values of copolymerization reactivity ratios, except in the case of pentahalogenostyrenes where the steric hindrance effect predominate [3, 5]. The influence of *o*-, *m*- or *p*-bromostyrene isomers on the polymerization reaction has been studied as well, and it was found that there is a large difference among their overall polymerization rate following the order $o > m > p$ as a results of mutual polar, steric, and resonance effect interactions [6]. Also, some work dealing with the homopolymerization of 2,4,5-tribromostyrene (TBSt) and its copolymerization with styrene in bulk condition [3] or in solutions [7] has been reported. Recently, the copolymerization of brominated styrenes, particularly dibromo- and tribromostyrene, has attracted special attention because they can be used as reactive monomeric brominated flame retardants for thermoplastics [8–10].

In continuation of our studies on brominated copolymers [11–13], this paper details the copolymerization kinetics of TBSt with styrene (St) and describes its reaction with acrylonitrile (AN) at low and high conversions in solution and discusses some properties of the copolymers obtained, particularly their thermal stabilities.



EXPERIMENTAL

Materials

Styrene was freed from inhibitor by washing with sodium hydroxide solution followed by several washings with water. It was dried over anhydrous sodium sulfate and distilled under nitrogen at 10 mm. Acrylonitrile was dried over anhydrous sodium sulfate and distilled at atmospheric pressure under nitrogen. 2,4,5-Tribromostyrene (Bromine Compounds, Ltd., Israel) was several times recrystallized from methanol, mp 67.5°C. The ^{1}H-NMR spectrum in $CDCl_3$ showed a doublet signals at δ 7.68 ppm and 7.73 ppm (phenyl), quartet signals at δ 6.68–7.05 ppm ($=CH_2$ group), and quartet signals at δ 5.38–5.79 ppm ($=CH$ group). 2,2′-Azobisisobutyronitrile (AIBN) was recrystallized from methanol. Solvents were purified in the usual manner.

Measurements

Thermogravimetric analyses (TG, DTA) were carried out with a DuPont 2000 and DCS-7 instrument in helium atmosphere and with a heating rate of 10°C/min. The compositions of copolymers were established by bromine analyses.

The molecular weights of the copolymers were measured by gel permeation chromatography (GPC) carried out on an Aerograph 8500 Varian instrument fitted with a UV detector. Styragel columns (Waters Associates) were used at a flow rate of 1 mL/min of degassed tetrahydrofuran. Retention times were calculated as polystyrene equivalents.

Intrinsic viscosities were measured on a Cannon-Fenske capillary viscometer No. 50 in chloroform at 30°C for TBSt and in tetrahydrofuran for TBSt-AN.

Polymerization Procedures

Solution polymerization to low conversion for the determination of the monomer reactivity ratios in toluene (50 mL solutions) of monomers (0.025 mol) with AIBN (0.082 g) as the initiator at 60°C were carried out under a constant stream of nitrogen in a 100-mL, double-jacketed glass reactor equipped with a magnetic stirrer. After an appropriate time interval (20-100 minutes), when a withdrawn sample precipitated in methanol, the whole reaction mixture was poured into methanol, and the polymer was isolated by filtration, dissolved in toluene, reprecipitated, and dried at 60°C and 0.1 mm.

Rates of copolymerization were measured dilatometrically. Dilatometers (about 20 mL) filled with the toluene solution of the monomer mixture and with the initiator (AIBN) were connected to a high vacuum line and freed of oxygen by three freezing-thawing cycles. The dilatometers were then placed on a thermostated bath, and the volume contraction was recorded as a function of time. The reaction was terminated by vacuum suction of the contents and precipitation in excess methanol. The conversion was determined gravimetrically.

RESULTS AND DISCUSSION

Copolymerization Reaction

The free radical copolymerization of 2,4,5-tribromostyrene (TBSt) with styrene (St) was performed in toluene solution using AIBN as the initiator. The influence of the molar fraction of TBSt in the initial monomer mixture (f) on the composition (F) of the resulting copolymers obtained at low conversions are summarized in Table 1. In both cases the plots of instantaneous monomer-copolymer mol fraction composition (Fig. 1) show a marked tendency toward a random copolymerization reaction, the TBSt content being higher in the copolymers. By using the Kelen-Tüdös equation [14], the copolymerization reactivity ratios and the confidence intervals were calculated and have been related to the polarity (e) and the resonance effect (Q) in the Alfrey-Price scheme (Table 2), assuming the values for St and AN giving in the literature [15]. Somewhat higher values for both parameters in styrene copolymerization were found by Oishi [7] and some lower by Cubbon [3]. Tribromostyrene is thus more reactive than St or AN toward both types of propagating species, and the resulting copolymers are therefore richer in TBSt than the monomer mixtures. The initial reaction rates, R_p, for different monomer feed ratios, but at a constant total monomer concentration (0.5 mol/L), are plotted in Fig. 2. They were determined by dilatometry at low conversion and they give straight lines in both cases, increasing as the content of brominated monomer in the

TABLE 1. Copolymerization of 2,4,5-Tribromostyrene (TBSt) (M_1) with Styrene (St) (M_2) or Acrylonitrile (AN) (M_2) in Toluene at 60°C with AIBN as Initiator[a]

f_1	TBSt-St conversion, %	Br, %	F_1	TBSt-AN conversion, %	Br, %	F_1
0.1	6.85	32.29	0.279	8.31	52.32	0.311
0.2	8.77	49.64	0.423	7.23	61.76	0.529
0.3	12.39	54.80	0.520	18.94	63.70	0.599
0.4	10.77	58.82	0.609	22.59	65.62	0.685
0.5	5.38	60.70	0.658	24.98	66.70	0.741
0.6	5.73	62.45	0.708	9.75	67.48	0.787
0.7	20.09	64.15	0.761	14.93	68.50	0.854
0.8	9.11	65.57	0.808	10.31	69.30	0.913

[a] Polymerization conditions: Toluene solution (50 mL) of monomers (0.025 mol) and AIBN (0.082 g) at 60°C.

monomer mixture increases from 0.1 to 0.8 mol fraction. This influence is somewhat stronger with AN as the comonomer. Figure 3 illustrates the dependence of R_p on $[\mathrm{AIBN}]^{0.5}$. A straight lines passing through the origin demonstrates bimolecular termination for both the copolymerization processes. The dependence of the initial copolymerization rate R_p on the monomer concentrations in the monomer mixture,

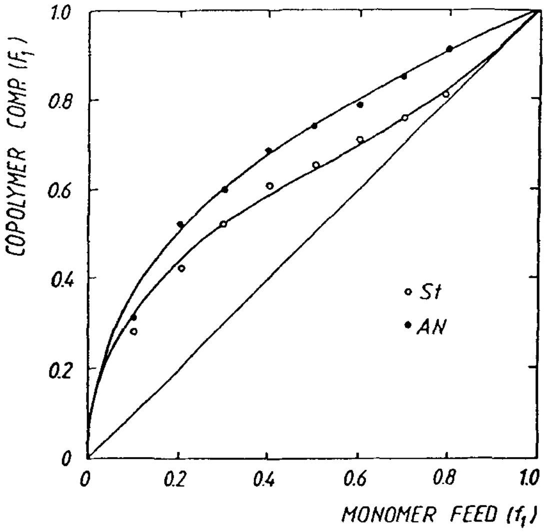


FIG. 1. Monomer-copolymer composition curves for the copolymerization of 2,4,5-tribromostyrene (TBSt) (M_1) with styrene (St) (M_2) or acrylonitrile (AN) (M_2) in toluene at 60°C with AIBN. Experimental (○); calculated by r_1 and r_2 (——).

TABLE 2. Copolymerization Parameters for Free-Radical Copolymerization of 2,4,5-Tribromostyrene (TBSt) (M_1) with Styrene (St) (M_2) or Acrylonitrile (AN) (M_2)

M_2	r_1	r_2	e_1	Q_1
St	1.035 ± 0.164	0.150 ± 0.057	0.56	2.24
AN	2.445 ± 0.270	0.133 ± 0.054	0.14	1.26

but at constant monomer molar compositions of 0.25 (TBSt) and 0.75 (St) or AN, is plotted in Fig. 4. The R_p of copolymerization increases linearly for both systems and, as expected, much higher reaction rates are obtained by increasing the total monomer concentration.

The course of the copolymerization of TBSt to high conversion in toluene is represented by the integrated time-conversion curves with St (Fig. 5) and AN

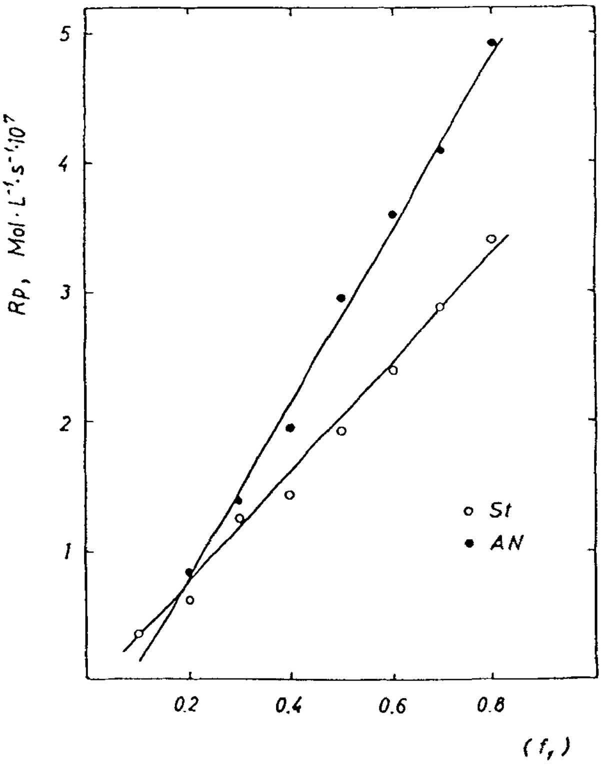


FIG. 2. Dependence of the initial reaction rates (R_p) on monomer feed composition (f_1) in the copolymerization of 2,4,5-tribromostyrene (TBSt) (M_1) with styrene (St) (M_2) or acrylonitrile (AN) (M_2) at a total monomer concentration of [M] = 0.5 mol/L, [AIBN] = 1×10^{-2} mol/L in toluene at 60°C.

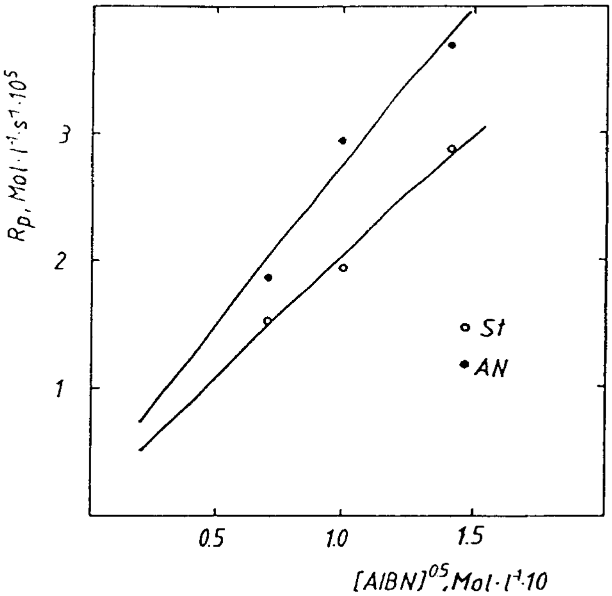


FIG. 3. Initial rate of copolymerization, R_p, of 2,4,5-tribromostyrene (TBSt) (M_1) with styrene (St) (M_2) or acrylonitrile (AN) (M_2) versus $[AIBN]^{0.5}$, total [M] = 0.5 mol/L, for the constant monomer feed composition (M_1/M_2 = 0.5/0.5) in toluene at 60°C.

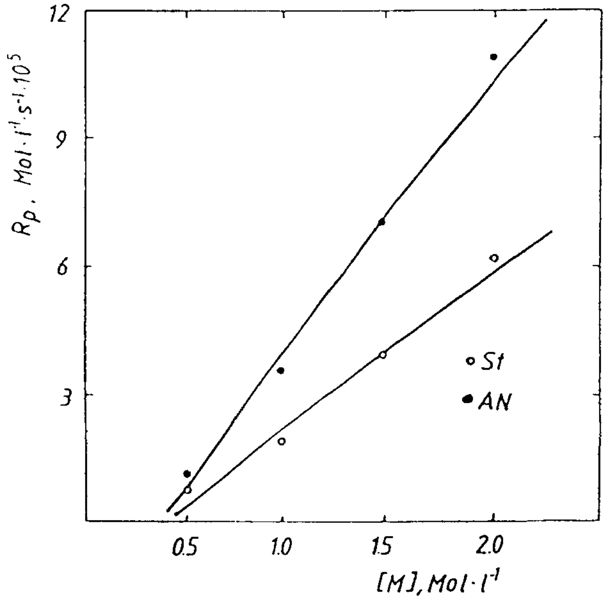


FIG. 4. Dependence of the initial reaction rate (R_p) of the copolymerization of 2,4,5-tribromostyrene (TBSt) (M_1) with styrene (St) (M_2) or acrylonitrile (AN) (M_2) on the total concentration of the monomer mixture [M] for the constant monomer feed composition (M_1/M_2 = 0.25/0.75), [AIBN] = 1×10^{-2} mol/L, in toluene at 60°C.

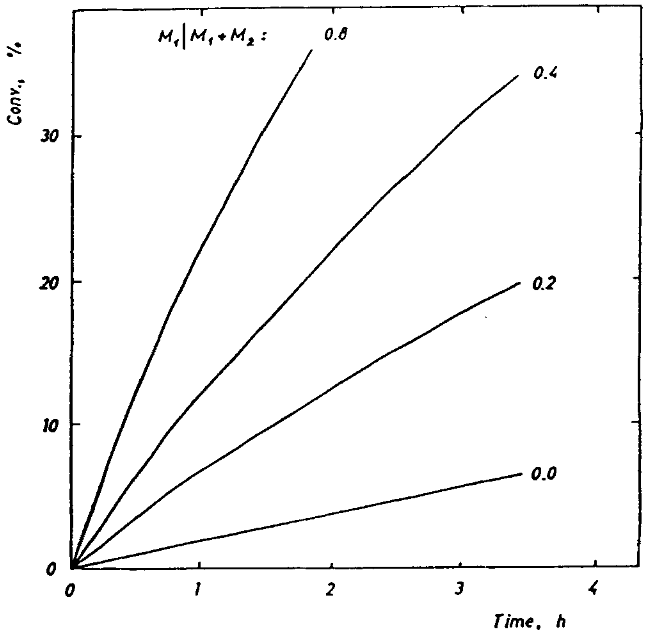


FIG. 5. Influence of the monomer mixture composition on conversion versus reaction time in the copolymerization of 2,4,5-tribromostyrene (TBSt) (M_1) and styrene (St) (M_2): [M] = 0.5 mol/L, [AIBN] = 1 × 10^{-2} mol/L, in toluene at 60°C.

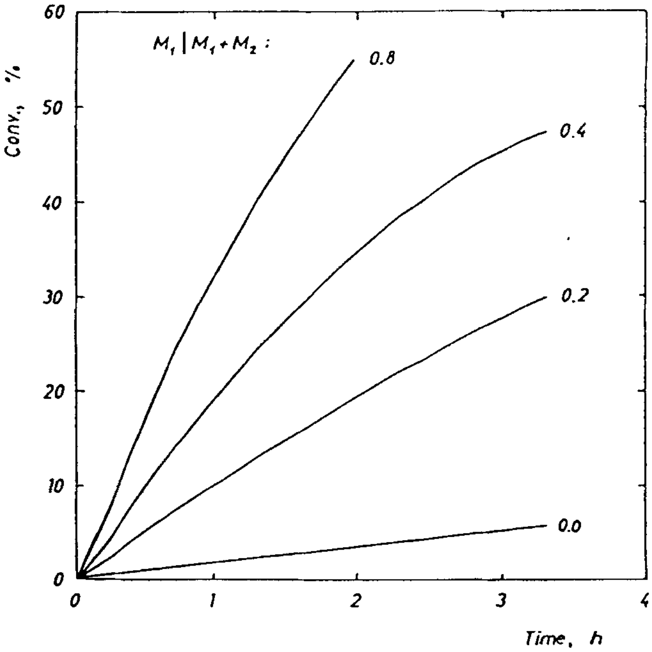


FIG. 6. Influence of the monomer mixture composition on conversion versus reaction time in the copolymerization of 2,4,5-tribromostyrene (TBSt) (M_1) and acrylonitrile (AN) (M_2): [M] = 0.5 mol/L, [AIBN] = 1 × 10^{-2} mol/L, in toluene at 60°C.

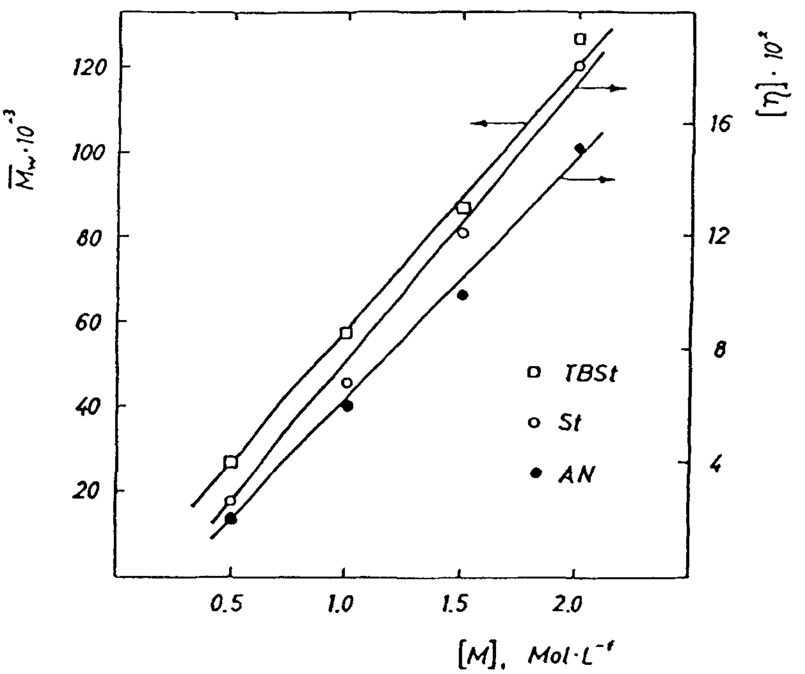


FIG. 7. Relation of molecular weight ($\overline{M}_w$) or intrinsic viscosity ($[\eta]$) of the copolymers obtained at low conversion (up to 10%) on the total monomer mixture concentration ([M]) in the copolymerization of 2,4,5-tribromostyrene (TBSt) (M_1) and styrene (St) (M_2) or acrylonitrile (AN) (M_2) for the total monomer feed composition ($M_1/M_2 = 0.25/0.75$), [AIBN] = 1×10^{-2} mol/L, in toluene at 60°C.

(Fig. 6) as comonomers. The familiar pattern of the curves shows an increase of conversion as the mole fraction of TBSt increases in the monomer mixture. Comparison of the examined polymerization systems shows that higher conversions were obtained with AN as a comonomer for the same reaction time. It is also well documented that the polymerization of acrylonitrile in bulk or in an aromatic solvent like benzene or toluene proceeds in heterogeneous condition owing to precipitation of the polymer formed [16]. In such a system an accelerated polymerization rate was observed. This phenomenon could have the same influence on the course of the TBSt-AN copolymerization reaction, particularly when a higher AN fraction in the monomer mixture was used.

Copolymer Properties

The molecular weight and intrinsic viscosity measurements on the copolymers obtained at constant monomer mixture (TBSt/St = 0.25/0.75), but different total monomer concentration at low conversion up to 10%, is plotted in Fig. 7. The $\overline{M}_w$ and $[\eta]$ for TBSt/St copolymers as well as $[\eta]$ for TBSt/AN copolymers increase linearly as the total monomer concentration increases from 0.5 to 2.0 mol/L. The observed findings are probably caused not only by the higher propagation reaction rates but also by the lower termination rates at higher monomer concentrations.

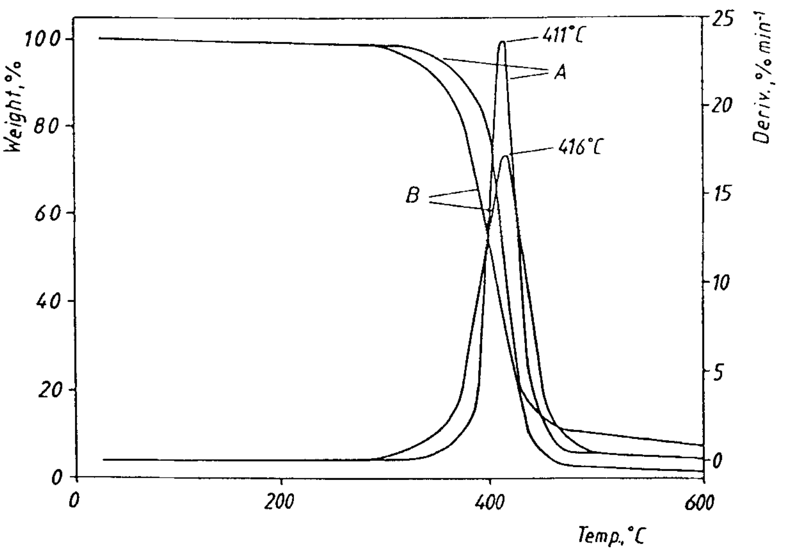


FIG. 8. Thermogravimetric analysis of poly(2,4,5-tribromostyrene) (A) and polystyrene (B) in helium.

The thermal properties of poly-TBSt, homopolymer, and both types of copolymers were determined by TGA and DTA measurements in a helium atmosphere. From the thermogravimetric curves of the homopolymer decompositions (Fig. 8), it is evident that the characteristic temperatures of the beginning and at the end of rapid decomposition of poly-TBSt are almost identical with that of polysty-

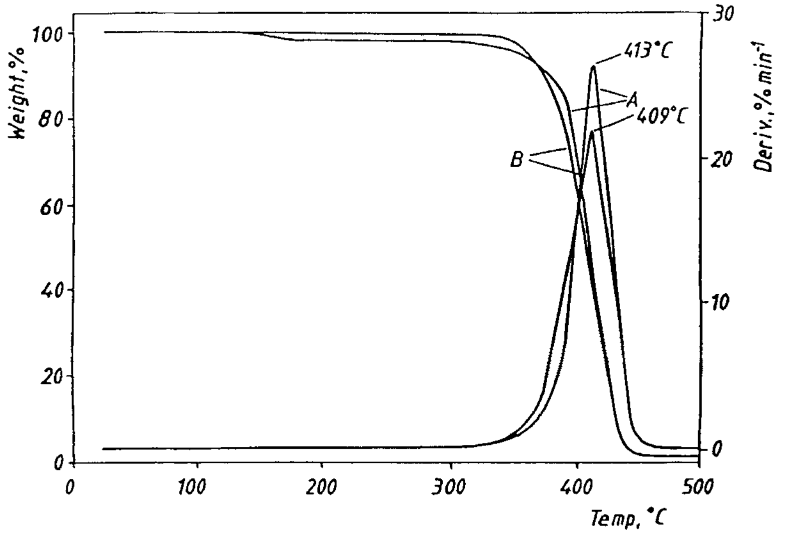


FIG. 9. Thermogravimetric analysis of copolymer of 2,4,5-tribromostyrene (TBSt) and styrene (St) in helium. Molar ratio: A = 0.48/0.52 and B = 0.58/0.42.

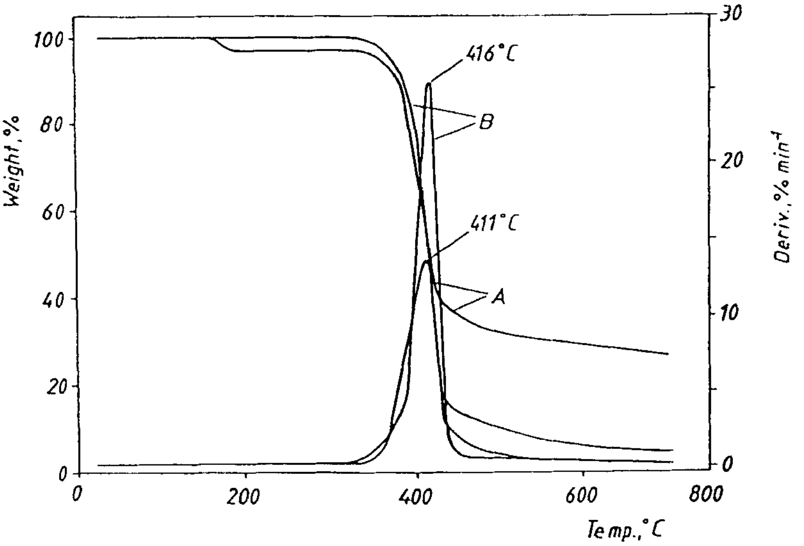


FIG. 10. Thermogravimetric analysis of copolymer of 2,4,5-tribromostyrene (TBSt) and acrylonitrile (AN) in helium. Molar ratio: A = 0.33/0.67 and B = 0.67/0.33.

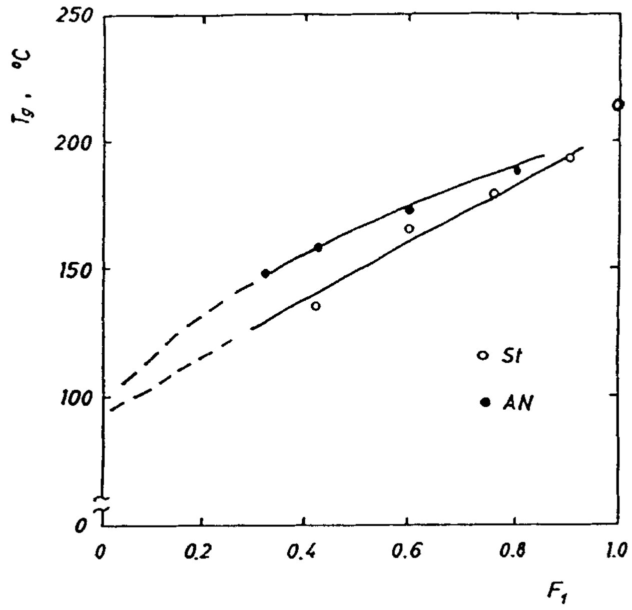


FIG. 11. Correlation of copolymer composition (F_1) and glass transition temperature (T_g) for 2,4,5-tribromostyrene–styrene (○) and 2,4,5-tribromostyrene-acrylonitrile copolymers (●).

rene. Some residue at the end of the fast decomposition region indicated that depolymerization to volatile monomers had not been complete. Typical thermograms of copolymers for the two different compositions for TBSt-St and TBSt-AN are shown in Figs. 9 and 10, respectively. They show similar decomposition curves, decomposing spontaneously at a temperature located about 10°C below the decomposition temperature of polystyrene. For both copolymers, however, the increasing of TBSt content does not improve significantly their thermal stability. The relatively higher residue content at the end of decomposition of TBSt-AN, increasing as the AN fraction increases in the copolymer, indicates that the decomposition did not go to completion, the usual characteristic of acrylonitrile-based polymers [17].

The glass transition temperatures (T_g), determined by DSC measurements over a wide range of copolymer composition and obtained at low copolymerization conversions, are shown in Fig. 11. A linear correlation between the molar fraction of TBSt in both copolymer samples and the glass transition temperature is obtained, and a value of 211°C for poly(2,4,5-tribromostyrene) is found by extrapolation. However, the value established experimentally was 217°C.

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