Polymer Bulletin 40, 651–658 (1998)

Polymer Bulletin

Radical polymerization of (phenylethynyl)styrenes and characterization of poly(phenylethynyl)styrenes as a thermally curable material

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Received: 28 January 1998/Accepted: 5 March 1998

Summary

The radical polymerizations of 2-, 3-, and 4-(phenylethynyl)styrenes (**1a-c**) and the copolymerizations of **1a-c** (M_1) with styrene (M_2) were carried out using AIBN as the initiator in toluene at 60 °C. The number-average molecular weights (M_ns) were extremely low for poly(2-phenylethynylstyrene) (**2a**) and poly[(phenylethynyl)styrene-*co*-styrene] (**3a**), and increased in the order of **2a, 3a** << **2b, 3b** < **2c, 3c**. Monomer reactivity ratios were determined as $r_1 = 1.80$ and $r_2 = 0.51$ for **1a**, $r_1 = 1.72$ and $r_2 = 0.53$ for **1b**, and $r_1 = 3.17$ and $r_2 = 0.24$ for **1c**. Polymers **2a-c** and **3a-c** underwent an exothermic reaction at elevated temperature to form organic solvent-insoluble polymers. Although the decomposition of **2a** was observed from 200 °C, **2b** and **2c** exhibited a high heat-resistance property in both nitrogen and air atmospheres, in particular, **2b** showed no significant weight loss below 450 °C.

Introduction

Polymers and oligomers containing ethynyl groups are materials of significant importance, because they can be thermally cured at moderately elevated temperatures without giving off volatiles to yield crosslinked thermally stable resins as suitable matrices for advanced composites (1). Therefore, it is interesting to design and synthesize a polymer with an ethynyl group as an attractive candidate for thermal curing materials (2), For example, a variety of polymers containing ethynyl groups at the chain termini have been widely studied (3). However, the polymer having the pendent ethynyl group, which is characterized as having a content of ethynyl groups that can be widely varied, has been only scarcely reported (4,5).

Previously, we reported that the radical polymerizations of (trimethylsilylethynyl)-styrenes and their uses with styrene produced gel-free polystyrenes with trimethylsilylethynyl groups. The deprotection of the silyl group in the poly(trimethylsilylethynyl)styrenes smoothly proceeded for conversion into polystyrenes having pendent ethynyl groups, and subsequently underwent curing reactions at elevated temperature to form crosslinking polystyrenes even though the content of the ethynyl group was extremely low (6). From the standpoint of practical use, therefore, it is important to synthesize a polymer having the pendent C≡C group for which the deprotection procedure is not required.

The present study reports the radical polymerizations of 2-, 3-, and 4-(phenylethynyl)styrenes (**1a-c**) and their copolymerizations with styrene. The copolymerization parameters, the monomer reactivity ratio and the *Q* and *e* values, are determined for **1a-c** as

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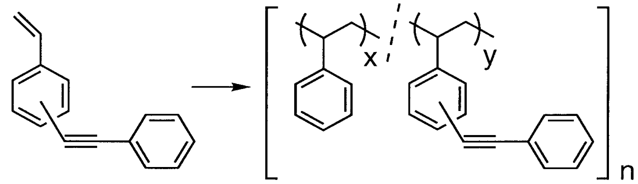
new styrene monomers and discussed together with the values for the 2-, 3-, and 4-ethynylstyrenes. Furthermore, the thermal crosslinking properties of poly[(phenylethynyl)-styrene] (**2a-c**) and poly[(phenylethynyl)styrene-*co*-styrene] (**3a-c**) at elevated temperature were characterized as a thermally curable material.



ortho	meta	para		ortho	meta	para
1a	**1b**	**1c**	Homopolymer	**2a**	**2b**	**2c**
			Copoymer	**3a**	**3b**	**3c**

Experimental

Measurements. Infrared and Raman spectra were recorded using a JEOL JIR RFX-4002F FT-IR spectrophotometer and a JASCO NR-1800 Raman spectrophotometer, respectively. ^{1}H and ^{13}C-NMR spectra were recorded using a Hitachi R-24B, JEOL JNM-EX270, and JEOL JNM-EX400 instruments. Size exclusion chromatograms (SEC) were obtained using a Showa Denko System-11 instrument equipped with three polystyrene gel columns (Shodex K-805L x 3) with refractive index detection at 40 °C. Chloroform was the carrier solvent at a flow rate of 1.0 mL/min. Differential scanning calorimetry (DSC) and thermal gravimetry (TG) measurements were carried out under N_2 gas using a Seiko DSC220 and a TG/DTA22 instrument, respectively. The heating scan rate was 10 °C/min for all experiments.

Materials. 2-, 3-, and 4-Bromostyrene were prepared as previously reported (6). Bis(triphenylphosphine)palladium(II) chloride was kindly supplied by N.E. Chemcat. Styrene, toluene, and triethylamine were purified by the usual methods. 2,2’-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. Commercially available phenylacetylene was used without further purification.

2-(Phenylethynyl)styrene (1a). A solution of 2-bromostyrene (35.0 g, 191 mmol), phenylacetylene (28.5 g, 279 mmol), copper(I) iodide (0.442 g, 2.32 mmol), and triphenylphosphine (0.570 g, 2.18 mmol) in dry triethylamine (285 mL) was bubbled with nitrogen for 1 h at room temperature. Bis(triphenylphosphine)palladium(II) chloride (1.39 g, 1.98 mmol) was added to the solution, and the mixture was stirred at 70 °C for an additional 76 h under an atmosphere of nitrogen. After filtration of the precipitated triethylaminium salt, the solvent was evaporated. The residue was diluted with hexane and washed with water, 2N HCl, and brine. The extract was then dried over anhydrous Na_2SO_4. After filtration and evaporation, column chromatography on silica gel (particle size, 0.063-0.200 mm) with hexane as the eluent yielded the desired product **1a**. It was further purified by fractional distillation at 138 - 141 °C (0.65 mmHg) to give 29.1 g (85.6 %) of **1a** as a yellow liquid. ^{1}H-NMR (270 MHz, $CDCl_3$): δ 5.38 (dd, 1H, *cis*-CH=CH$_2$, *J* = 10.92 and 0.95 Hz), 5.85 (dd, 1H, *trans*-CH=CH$_2$, *J* = 17.52 and 0.81 Hz), 7.20 - 7.62 (m, 10H, Ar-H and CH=); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 87.82 and 94.06 (C≡C), 115.67 (=CH$_2$), 122.01 (ArC2), 123.41 (ArC1'), 124.75 (ArC6), 127.57 (ArC4), 128.41 (ARC5), 128.45 (ArC3'), 128.53 (ArC4'), 131.63 (ArC2'), 132.59 (ArC3), 135.03 (CH=), 139.07 (ArC1); IR (neat): 914 (CH=CH$_2$), 2213 cm^{-1} (C≡C); Anal. calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92; found: C, 94.26; H, 5.87.

3-(Phenylethynyl)styrene (1b). This procedure is similar to that used for the preparation of

1a. From 3-bromostyrene (47.09 g, 257 mmol) and phenylacetylene (31.50 g, 309 mmol), the crude product isolated by column chromatography was recrystallized from hexane at -30 °C and then distilled at 115 - 124 °C (0.2 mmHg) to give 30.4 g (58.0 %) of **1b** as white crystals (m.p. 36.0 - 37.5 °C): ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.29 (d, 1H, *cis*-$CH{=}CH_2$, *J* = 11.00 Hz), 5.78 (d, 1H, *trans*-$CH{=}CH_2$, *J* = 17.56 Hz), 6.70 (dd, 1H, CH=, *J* = 11.00 and 17.56 Hz), 7.60 - 7.27 (m, 9H, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 89.31 and 89.47 ($C{\equiv}C$), 114.79 (=CH_2), 123.27 (ArC3), 123.58 (ArC1'), 126.22 (ArC6), 128.38 (ArC5), 128.43 (ArC3'), 128.63 (ArC4'), 129.46 (ArC2), 130.94 (ArC4), 131.70 (ArC2'), 136.18 (CH=), 137.81 (ARC1); IR (neat): 920 ($CH{=}CH_2$), 2206 cm^{-1} ($C{\equiv}C$); Anal. calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92; found: C, 94.11; H, 5.95.

4-(Phenylethynyl)styrene (1c). This procedure is similar to that used for the preparation of **1a**. From 4-bromostyrene (47.09 g, 257 mmol) and phenylacetylene (31.50 g, 309 mmol), the crude product isolated by column chromatography was purified by recrystallization from hexane to give 20 g (52 %) of **1c** as white crystals (m.p. 81.3 - 82.0 °C). ^{1}H-NMR (270 MHz, $CDCl_3$): δ 5.29 (d, 1H, *cis* -$CH{=}CH_2$, *J* = 10.9 Hz), 5.77 (d, 1H, *trans* -$CH{=}CH_2$, *J* = 17.5 Hz), 6.70 (dd, 1H, CH=, *J* = 10.9 and 17.5 Hz), 7.55 - 7.32 (m, 9H, Ar); ^{13}C-NMR (67.9 MHz, $CDCl_3$): δ 89.52 and 90.15 ($C{\equiv}C$), 114.84 (=CH_2), 122.63 (ArC4), 123.37 (ArC1'), 126.25 (ArC2), 128.35 (ArC4'), 128.44 (ArC3'), 131.67 (ArC3), 131.87 (ArC2'), 136.34 (CH=), 137.53 (ArC1); IR (neat): 904 ($CH{=}CH_2$), 2218 cm^{-1} ($C{\equiv}C$); Anal. calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92; found: C, 93.85; H, 5.89.

Polymerization. Radical homo- and copolymerizations were carried out using AIBN as the initiator in toluene at 60 °C in sealed tubes under nitrogen gas. After polymerization, the solution was poured into a large amount of methanol. The precipitated polymers were purified by two reprecipitations from a THF/methanol system and freeze-dried from a benzene solution. **2a**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.7 - 4.0 (br m, 3H, CH_2CH), 5.8 - 8.2 (br s, 9H, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 37.0 ($CHCH_2$) 88.4 and 92.8 ($C{\equiv}C$), 123.5 (ArC2 and 1'), 125.5 (ArC4 and 6), 128.1 (ArC5, 3', and 4'), 131.7 (ArC3 and 2'), 146.6 (ArC1); IR (neat): 2214 cm^{-1} ($C{\equiv}C$); Raman: 2216 cm^{-1} ($C{\equiv}C$); Anal. calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92; found: C, 94.09; H, 5.93. **2b**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 0.7 - 2.4 (br m, 3H, CH_2CH), 6.1 - 7.7 (br s, 9H, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 40.5 (CH_2), 43.3 (CH), 89.2 and 90.0 ($C{\equiv}C$), 123.0 (ArC3), 123.5 (ArC1'), 128.0 (ArC6), 128.4 (ArC5, C3' and C4'), 129.5 (ArC4), 130.9 (ArC2), 131.7 (ArC2'), 144.9 (ArC1); IR (neat): 2214 cm^{-1} ($C{\equiv}C$); Raman: 2216 cm-1 ($C{\equiv}C$); Anal. calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92; found: C, 94.26; H, 6.09. **2c**: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.0 - 2.2 (br m, 3H, CH_2CH), 6.2 - 7.7 (br s, 9H, Ar-H); ^{13}C-NMR (100 MHz, $CDCl_3$): δ 40.5 (CH_2), 43.3 (CH), 89.0 and 89.7 ($C{\equiv}C$), 120.9 (ArC4), 123.6 (ArC1'), 127.7 (ArC2), 128.0 (ArC4'), 128.3 (ArC3'), 131.7 (ArC3 and 2'), 144.9 (ARC1); IR (neat): 2216 cm^{-1} ($C{\equiv}C$); Raman: 2223 cm^{-1} ($C{\equiv}C$); Anal. calcd. for $C_{16}H_{12}$: C, 94.08; H, 5.92; found: C, 94. 10; H, 6.12.

Results and Discussion

Radical polymerization of 1a-c

The homo- and copolymerizations of **1** with AIBN were carried out at 60 °C in toluene. Table 1 summarizes the results of the polymerizations of the 2-, 3-, and 4-(phenylethynyl)styrenes (**1a-c**) and their copolymerizations with styrene. All the polymerizations proceeded homogeneously and the obtained polymers, **2a-c** and **3a-c**, were soluble in common organic solvents such as benzene, THF, and chloroform and insoluble in methanol. The SEC chromatograms for all the polymer samples showed a unimodal peak. The number-average molecular weights (M_ns) were extremely low for the 2-phenylethynyl substituted polystyrenes, **2a** and **3a**, and increased in the order of **2a, 3a** << **2b, 3b** < **2c, 3c**. The

Table 1. Radical polymerization of 2-, 3,- and 4-(phenylethynyl)styrenes (**1a-c**) (M_1) without/with styrene (M_2) [a]

polymer	mole fraction of M_1 in monomer feed	time h	yield %	mole fraction of M_1 unit in copolymer[b]	$M_n(M_w/M_n)$[c]
2a	1.00	48	31	1.00	1,470 (1.13)
3a	0.49	48	28	0.57	1,690 (1.20)
3a	0.10	48	32	0.10	3,360 (1.33)
2b	1.00	22	40	1.00	13,300 (1.97)
3b	0.49	49.5	34	0.49	11,000 (1.92)
3b	0.10	23	60	0.10	14,600 (1.72)
2c	1.00	3.5	36	1.00	70,200 (1.61)
3c	0.50	13	61	0.78	35,600 (1.98)
3c	0.05	13.5	58	0.11	20,000 (1.67)

a) Initiator, AIBN; $[M_1]$ or $[M_1 + M_2] = 5.0\ \mathrm{mol \cdot L^{-1}}$; $[\mathrm{AIBN}] = 50\ \mathrm{mmol \cdot L^{-1}}$; temp. 60 °C; solvent, toluene. b) Determined by ^{1}H NMR spectra. c) Determined by SEC using polystyrene standard.

lowest and highest M_n was 1,470 for **2a** and 70,200 for **2c**. The introduction of a styrene unit in **2a** caused an increase in the M_ns though they were still low, whereas the M_ns of **3c** were lower than that of **2c**. A similar tendency for the M_ns was observed for the homo- and copolymers obtained by the radical polymerization of the 2-, 3-, and 4-(trimethylsilylethynyl)styrenes (**4a, 4b,** and **4c**, respectively) (6). These low M_ns of the 2-ethynyl substituted monomers could be caused by the chain transfer reactions during the radical polymerization.

The characteristic absorptions due to the ethynyl group were observed at 89.2 and 90.0 ppm in the ^{13}C-NMR spectrum of **2b**, as shown in Figure 1. In addition, the absorption due to the C≡C group was also observed at 2216 cm^{-1} in the Raman spectrum though that at 2214 cm^{-1} in the IR spectrum was very weak. These results indicate that no influence by the carbon-carbon triple bond occurred during the radical polymerization.

Figure 2 shows the copolymerization composition curves for **1** (M_1) and styrene (M_2). The copolymerization yield in each run was less than 20 %. The copolymer compositions of **1a-c** and styrene were determined by the ratio of the adsorptions at 1 - 3 ppm and 6

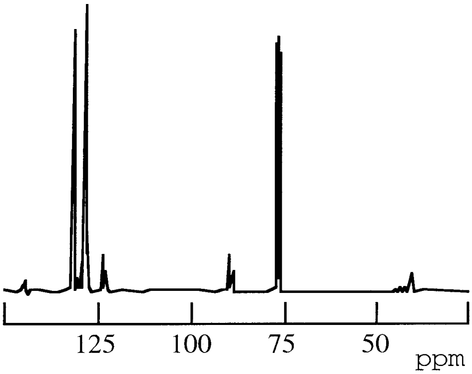


Figure 1. ^{13}C-NMR spectrum of poly[(3-phenylethynyl)styrene] (**2b**) .

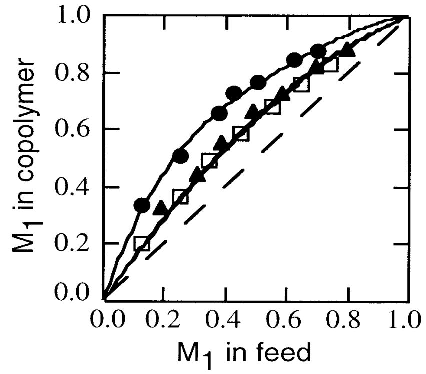


Figure 2. Composition curves for the copolymerizations of 2-(phenylethynyl)styrene (**1a**) with styrene (▲), 3-(phenylethynyl)styrene (**1b**) with styrene (□), and 4-(phenylethynyl)styrene (**1c**) with styrene (●).

- 8 ppm due to the methine and methylene protons and the aromatic protons, respectively, in their ^{1}H-NMR spectra. Monomer reactivity ratios, which are determined according to the high conversion method reported by Tüdõs *et al.* (7), are r_1 = 1.80 and r_2 = 0.51 for **1a**, r_1 = 1.72 and r_2 = 0.53 for **1b**, and r_1 = 3.17 and r_2 = 0.24 for **1c**. The reactivity of **1c** toward the polystyryl radical, which can be estimated using the $1/r_2$ value, is higher than those of **1a** and **1b**, which is similar to the result for **4a-c**. In Table 2, Q_1 and the e_1 values, which were calculated assuming Q_2 = 1.0 and e_2 = -0.8 for styrene, are compared with those of the **4a-c. 1a-c** were found to be conjugative and electron withdrawing monomers, as well as **4a-c**. The electron withdrawing character of the phenylethynyl group is indicated by the Hammett values, *i.e.*, σ_m = 0.14 and σ_p = 0.16 (8).

Table 2. Monomer reactivity ratios (r_1 and r_2) and Q_1 and e_1 values for (phenylethynyl)styrenes (M_1) and styrene (M_2) [a)]

M_1	r_1	r_2 ($1/r_2$)	Q_1	e_1
1a	1.80	0.51 (1.96)	1.56	-0.53
1b	1.72	0.53 (1.89)	1.48	-0.49
1c	3.17	0.24 (4.17)	2.74	-0.28
4a [b)]	1.22 [c)]	0.51 (1.96) [c)]	1.13 [c)]	-0.12 [c)]
4b [b)]	1.05 [c)]	0.82 (1.21) [c)]	0.95 [c)]	-0.42 [c)]
4c [b)]	1.39 [c)]	0.34 (2.56) [c)]	1.47 [c)]	0.07 [c)]

a) Calculated according to the high conversion method reported by Tüdõs *et al.* (7). b) **4a**, **4b**, and **4c** are 2-, 3-, and 4-(trimethylsilylethynyl)styrene, respectively. c) See ref. 6 (a), recalculated by the high conversion method (7).

Thermal properties of 2a-c and 3a-c

For the DSC thermograrn of **2b**, the endothermic peak corresponding to a glass transition temperature (T_g) was observed at 118 °C, as shown in Figure 3. The large exothermic peak appeared at 294°C with a top peak temperature of 366 °C which was not observed during the 2nd heating. In addition, after the 1st heating, the absorption at 2216 cm^{-1} due to

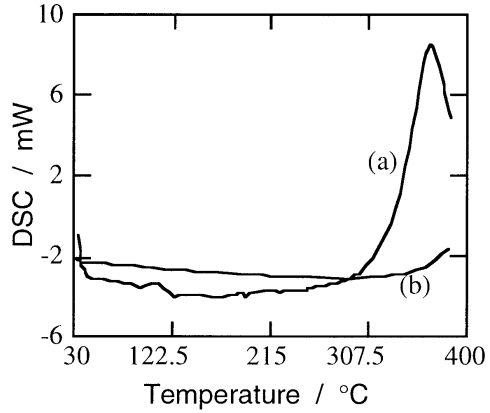


Figure 3. 1st heating (a) and 2nd heating (b) of poly[(3-phenylethynyl)styrene] (**2b**).

the ethynyl group completely disappeared in the Raman spectrum, as shown in Figure 4, and the annealed **2b** was insoluble in benzene, THF, chloroform, DMF, and DMSO. These results indicated that the exothermic peak between 294 °C and 440 °C was due to the crosslinking reaction of the ethynyl groups.

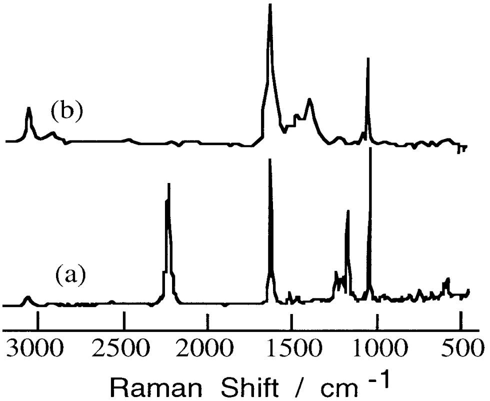


Figure 4. Raman spectra of poly[(3-phenylethynyl)styrene] (**2b**) (a) and crosslinked **2b** (b).

Table 3 summarizes the T_g, the temperature of 10 % weight loss (T_d), and the beginning temperature of the crosslinking reaction (T_r) and its top peak temperature in parenthesis for **2** and **3**. The T_g decreased with increasing St units for each **2/3** system. For the **2a/3a** system, the T_ds were lower than their top peak T_rs which decreased with increasing St units, *i.e.*, the thermal decomposition of polymers occurred before the crosslinking reaction. This result should be caused by the low molecular weights of **2a/3a**. The T_r increased with increasing St units, *i.e.*, from 294 to 313 °C for **2b/3b** and from 276 to 319 °C for **2c/3c**. In addition, the T_ds from 383 to 491 °C for **2b/3b** and from 388 to 476 °C for **2c/3c** were higher than that of poly(styrene) M_n = 19500 and M_w/M_n = 1.54) obtained by a radical polymerization, T_d = 362 °C. Figure 5 shows the TG curves of **2a-c**. Although the decomposition of **2a** was observed from 200 °C, **2b** and **2c** each exhibited a high heat-resistance property in both nitrogen and air atmospheres, in particular, **2b** showed no significant weight loss below 450

Table 3. Thermal properties of poly(phenylethynyl)styrene (**2**) poly[(phenylethynyl)styrene-*co*-styrene] (**3**)

polymer	mole fraction of M_1 unit in copolymer	T_g (°C)	T_r [a] (°C)	T_d [b] (°C)
2a	1.0	99	309 (389)	365
3a	0.57	95	298 (370)	343
3a	0.10	94	240 (335)	331
2b	1.0	118	294 (366)	491
3b	0.49	110	298 (380)	421
3b	0.10	96	313 (386)	383
2c	1.0	148	276 (363)	476
3c	0.78	146	296 (369)	433
3c	0.11	104	319 (382)	388

a) Beginning temperature of crosslinking reaction (top peak temperature of exothermic peak).
b) Temperature of 10 % weight loss.

°C and the T_d of **2b** was obtained at the high temperature of 491 °C. Furthermore, the T_ds of **2b** and **2c** were about 40 °C higher than that of polystyrenes having pendent ethynyl groups, *i.e.*, the T_d was 452 °C for poly(3-ethynylstyrene) and 428 °C for poly(4-ethynyl styrene). Thus the thermal characteristics of polystyrenes having pendent C≡C groups, in particular, the heat-resistance property was improved by the introduction of the phenylethynyl group in styrene compared with poly(ethynylstyrene).

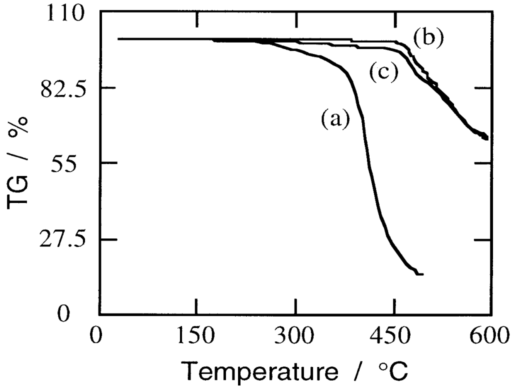


Figure 5. TG thermograms of poly[(2-phenylethynyl)styrene] (**2a**) (a), poly[(3-phenylethynyl)styrene] (**2b**) (b), and poly[(4-phenylethynyl)styrene] (**2c**) (c).

Conclusion

The radical polymerizations of (phenylethynyl)styrene and its use with styrene produced linear polystyrene with phenylethynyl groups. The polystyrenes having pendent phenylethynyl groups underwent curing reactions at elevated temperature to form crosslinking polystyrenes. In spite of the steric hindrance of the diphenyl substituted ethynyl group, complete disappearance of the carbon-carbon triple bond was ascertained in the annealed polymers. The thermal stability was improved by replacement of the terminal ethynyl group by the phenylethynyl group.

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