Rheological Characterization of Styrene Acrylonitrile Copolymers

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ABSTRACT: The relationship between copolymer composition, molecular weight distribution, and rheological properties of random styrene acrylonitrile copolymers synthesized by radical polymerization in bulk was investigated. From differential scanning calorimetry analysis, glass transition temperature was obtained and increases with the acrylonitrile content. The knowledge of the glass transition is a key factor to compare the different copolymers in an iso-free volume condition for melt rheology. Owing to time temperature superposition, a large frequencies window ranging from the terminal zone until the glassy plateau can be obtained. Thus, the mechanical spectroscopy was used to estimate the rubbery plateau modulus and the Newtonian viscosity. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1316–1321, 2000

Key words: SAN copolymers; rheological behavior; rubbery plateau modulus

INTRODUCTION

The properties of the styrene acrylonitrile (SAN) copolymers are influenced by their composition. These copolymers are synthesized in bulk or in the presence of various solvents such as acetonitrile or toluene. The comparison of the bulk systems with those involving toluene and acetonitrile has revealed a relatively small solvent effect.[1]

SAN copolymers are expected to be random copolymers with linear structure,[2,3] having the following reactivity ratio at 60°C : $rs_t = 0.4$ and $r_{AN} = 0.02$.

The purpose of this study was to understand the influence of the composition and the molecular weight distribution of the SAN copolymers on rheological characteristics and particularly on the rubbery plateau modulus and the Newtonian viscosity.

To compare the different SANs in an iso-free volume or iso-segmental friction factor condition, the rheological behavior should be considered at an iso-$(T - T_g)$ temperature.

A study of the glass transition of the copolymers was performed by means of the differential scanning calorimetry analysis.

EXPERIMENTAL

Synthesis and Characterization

Styrene and acrylonitrile monomers were obtained from Acros Organics Society (Geel, Belgium) and purified by distillation at reduced pressure. Radical initiated polymerization of styrene with acrylonitrile was performed in the presence of 2,2′-azobisisobutyronitrile (2‰) at 70°C with agitation. The polymeric products were purified after dissolving, precipitated in chloroform/meth-

anol (volume ratio 1:8), and dried in vacuum at 80°C.
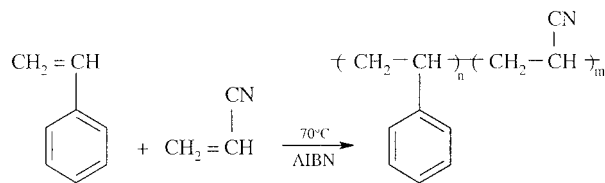
^{1}H-NMR spectra were recorded using a Brucker DRX 400 (400MH$_z$) spectrometer with CDCl$_3$ as solvent. The compositions for different monomer feed ratios were determined by ^{1}H-NMR and are given in Table I. These results were obtained by comparison between the aromatic and CH$_2$—CH proton signals which appears at different chemical displacements (aromatic proton characteristic from styrene units: 6.5–7.4 ppm and CH$_2$—CH protons: 1.2—2.7 ppm). Considering a chain with n styrene units and m acrylonitrile units, the styrene content can be obtained from the area of the signal due to aromatic protons in relation to the total area of the proton signal:

$$\text{Mol \% styrene} = \frac{5n}{8n + 3m}$$

$$= \frac{\text{Area of aromatic signal}}{\text{Total area of protons signal}} \quad (1)$$

$$\text{With } n + m = 1 \quad (2)$$

The solution of these equations gives the molar proportions (n, m); the mass proportions are given by the relation:

$$\text{wt \% styrene} = \frac{n \cdot Ms_t}{n \cdot Ms_t + m \cdot M_{AN}} \quad (3)$$

Ms_t = molar mass of styrene monomer = 104 g/mol. M_{AN} = molar mass of acrylonitrile monomer = 53 g/mol.

Size exclusion chromatography (SEC) was performed using a Waters 150 CV system including a differential refractive index detector; ultrastyragel columns (linear variation of porosity from 50 to 100,000 Å) and tetrahydrofuran (THF) as the eluent were used. Monodisperse polystyrene (PS) standards allowed the determination of the calibration curve. Values of average molecular weights and polydispersity indices are summarized in Table I. The SAN copolymers synthesized were studied as well as a PS homopolymer supplied by CdF Chimie, whereas in the case of polyacrylonitrile (PAN) homopolymer, no experiment was performed. Indeed, PAN tends to degrade well below its melting point because it undergoes exothermic cyclization. Generally, it is believed that PAN melt only at very high heating rates [i.e., 80°C min-1 (melting point 340°C) or above] under a nitrogen atmosphere, whereas at slow heating rates they degrade before melting.[4–9] This thermal behavior leads very difficult processing.

## Differential Scanning Calorimetry Analysis

Differential scanning calorimetry analysis was performed to determine the glass transition temperature using a Setaram 141 DSC at a rate of 10°C/min from 20 to 180°C. To avoid any difference in the thermal history, each sample was molten and cooled before the determination of the glass transition temperature.

Oscillatory Shear Flow

The preparation of the samples of SAN copolymers for dynamic oscillatory measurements in the melt was performed by compression molding

Table I Physical and Chemical Properties of the SAN Copolymers and of PS

Sample	Content of Styrene in the Feed (wt %)	Content of Styrene in the Copolymer by ^{1}H-NMR (wt %)	M_w (g/mol)	Polydispersity Index, I_p	M_n (g/mol)
SAN95	95	94.6	226,000	4.0	56,500
SAN85	85	85.5	413,000	4.1	100,700
SAN75	75	76	397,000	4.2	94,500
PS	100	100	234,000	3.6	64,000
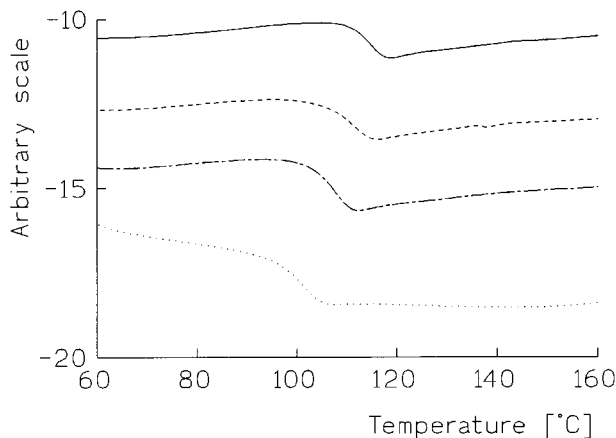
Figure 1 Thermograms for SAN copolymers and PS (—.—, SAN95; - - -, SAN85; —, SAN75; . . . , PS).

Figure 2 Shift factors for SAN copolymers (□, SAN95; *, SAN85; +, SAN75).

at T_g + 50°C to process disks of 25-mm diameter and 1-mm thickness. Rheological measurements in the melt were obtained in oscillatory mode using a disk and plate geometry in a rheometric dynamic spectrometer RDA 700. The storage modulus G' and the loss modulus G'' were measured at different temperatures from T_g + 5°C to high temperature in the frequency range 0.01 to 500 rad · s^{-1} after checking the linear viscoelastic domain. In the case of the lowest temperature (T_g + 5°C), the sample was heated at a higher temperature and then cooled to the temperature of the experiment.
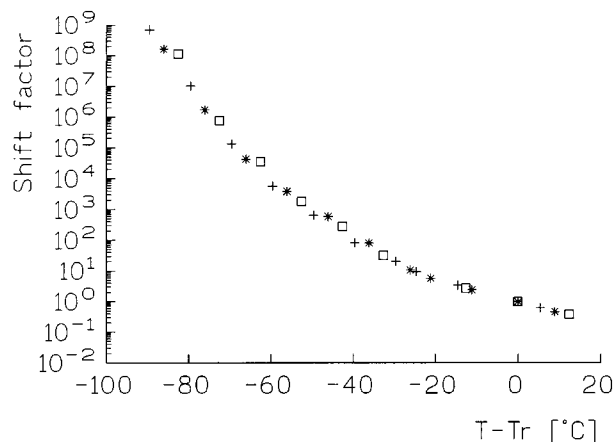
RESULTS AND DISCUSSION

Glass Transition

Figure 1 shows the thermogram of the SAN copolymers and PS. As expected, the glass transition temperature is sensitive to the level of acrylonitrile in the copolymer[10] and increases as the acrylonitrile content increases (Table II).

Table II   Glass Transition Temperature (T_g) and Reference Temperature (T_r) of the SAN Copolymers and of PS

| Reference	T_g (°C)	T_r (°C)
SAN95	107.6	187.6
SAN85	111.1	191.1
SAN75	114.6	194.6
PS	101	181

Surprisingly, the glass transition temperature for the SAN copolymers are slightly higher than those of PS (101°C, measured in our DSC) and PAN (106°C, found in the literature.[3] Theoretically, the glass transition temperature of random copolymers is expected between those of the homopolymers because copolymers tend to have intermediate chain stiffness and interchain attraction.[11]

However, such a discrepancy was also observed by Motta on similar materials.[3] Indeed, the presence of polar groups such as nitriles might raise the glass transition more than nonpolar groups with equivalent size, because of the restriction of rotation though polar interactions which is enhanced when the acrylonitrile content increases and the discrepancy was attributed to dipole attraction that can occur between different comonomer constituents and are not present between similar constituents.[3]

Shift Factors and Time Temperature Superposition

Measurements in oscillatory shear flow in the melt were performed at different temperatures ranging from T_g + 5°C to high temperature.

The determination of shift factors for time temperature superposition on each sample was performed to obtain master curves at a reference temperature which varied with the acrylonitrile content in copolymers to keep T_r − T_g constant (Table II). As can be seen from Figure 2, the plot of the shift factors versus temperature gives a single curve regardless of the composition of the SAN copolymers. Because of the difference of the glass transition temperature and the single curve
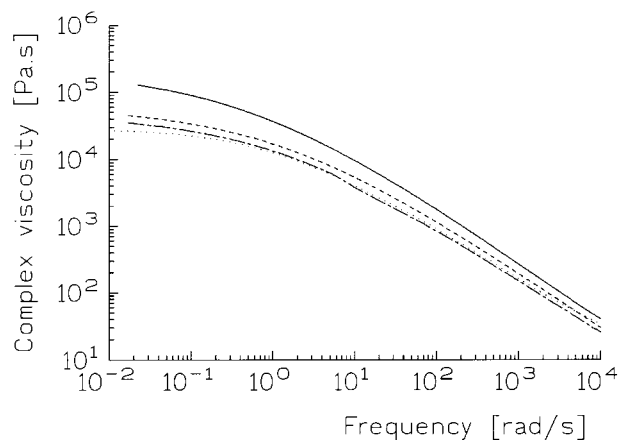
Figure 3 Complex dynamic viscosity for SAN copolymers and PS (—·—, SAN95; - - -, SAN85; —, SAN75; . . . , PS).

Figure 4 Storage modulus for SAN copolymers and PS (—·—), SAN95; - - -, SAN85; —, SAN75; . . . , PS).

of the shift factor, it is relevant to compare the rheological behavior in the melt of the samples at different reference temperatures which may be a necessary condition to obtain the iso-free volume condition. The understanding of the influence of the various structural parameters can only be performed from such comparisons.
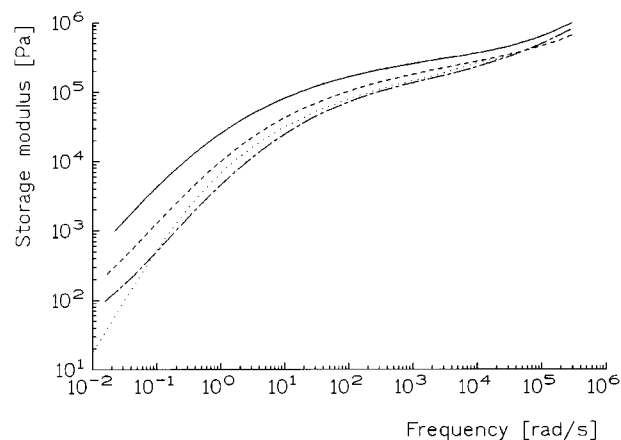
Newtonian Viscosity

Figure 3 shows the plots of the complex viscosity η^* versus frequency for the samples at the reference temperature in the molten state. The comparison should be made in an iso-free volume; the rheological behavior should thus be considered at an iso-$(T - T_g)$ temperature. In this study, $T - T_g$ was equal to 80°C.

The Newtonian viscosities η_0 at reference temperature are given in Table III. Despite the fact that SAN75 and SAN85 have a molecular weight distribution rather identical, the Newtonian viscosity of SAN75 is much higher than that of SAN85; this rheological parameter is influenced by the composition and increases with the acrylonitrile content. This should normally be reflected

Table III   Newtonian Limit Viscosity of the SAN Copolymers and of PS

Reference	η_O (Pa · s)
SAN95	3.51 (10^4)
SAN85	4.50 (10^4)
SAN75	12.79 (10^4)
PS	2.84 (10^4)

in the level of the plateau modulus which is not susceptible to the molecular weight distribution of the polymer.

Because of their rather identical molecular weight distribution, SAN95 and PS have nearly the same evolution of the complex viscosity. The highest value of the Newtonian viscosity for SAN95 can be explained by the presence of acrylonitrile.

Plateau Modulus

The rubbery plateau modulus (G_N^0) was determined from the experimental curve of the storage modulus G'. Indeed, as can be seen in Figure 4, the plot of the storage modulus versus frequency shows that the rubbery plateau is well pronounced.

Though the value of this plateau seems to be influenced by the composition of the copolymer, and it is higher when the acrylonitrile content is increased, the determination of the exact value on the plot of the storage modulus versus frequency remains difficult because G' slightly increases with the frequency in the plateau zone.

Different methods have been found in the literature to obtain an accurate value of the plateau. For example, Marin[12] proposes to determine G_N^0 at a frequency that corresponds to the geometric average of the frequencies of two successive intersections of the storage and the loss moduli in the terminal and plateau zones (middle of the width of the plateau). Values obtained by this method for our SAN are given in Table IV. As an example, Figure 5 shows the storage and the loss moduli for SAN85 and the various crossing points.

Table IV   Rubbery Plateau Modulus and Molecular Weight Between Entanglements of the SAN Copolymers and of PS

Reference	G_N° (MPa) in the Middle of $G'G''$ Intersections	G_N° (MPa) at the Minimum of tan δ	Percent Difference	M_e (g/mol) from G_N° in the Middle of $G'G''$ Intersections	M_e (g/mol) from G_N° at the Minimum of tan δ
SAN95	0.124	0.135	8.9	30,200	27,800
SAN85	0.188	0.187	0.5	20,400	20,500
SAN75	0.237	0.248	4.6	16,500	15,800
PS	0.106	0.113	6.6	34,700	32,700

Alternatively, some authors[13–17] have proposed that the value of the storage modulus G' at the minimum of the loss factor tan δ in the plateau zone may be a simple and reliable way to
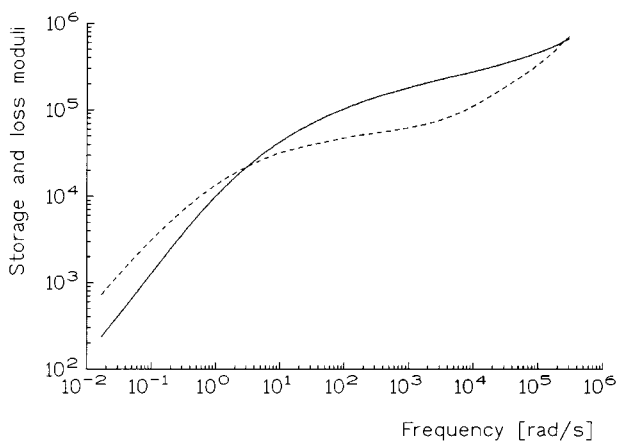
Figure 5   Storage and loss moduli for SAN85 (—G'; - - -, G'').
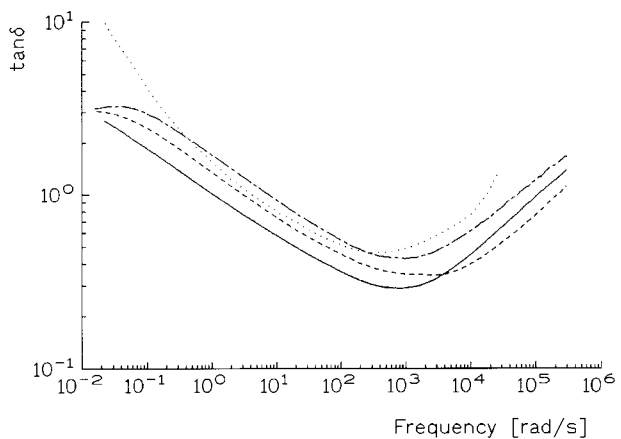
Figure 6   tan δ for SAN copolymers and PS (—.—, SAN95; - - -, SAN85; —, SAN75; . . . , PS).

estimate G_N^0. The evolution of tan δ for the SAN copolymers and PS is given in Figure 6. The corresponding values of the plateau modulus are given in Table IV. These two different methods of determination of the rubbery plateau modulus give approximately the same result, the maximum of difference ranging between 0.5 and 8.9%.

Different values of the rubbery plateau for PS are found in the literature: 0.2 Mpa,[12] 0.17 Mpa,[18,19] or 0.13 Mpa.[20,21] The latter value is now generally acknowledged, and is also consistent with the value obtained for our PS. Alternatively, Pfragnee and Schurz[22] have found $G_N^0 = 1$ MPa for PAN.[22] This confirms the fact that the plateau modulus of the SAN copolymers depends on their chemical composition.

From the plateau modulus it is possible to determine the molecular weight between entanglements M_e through the well known equation derived from the kinetic theory of rubber elasticity[23]:
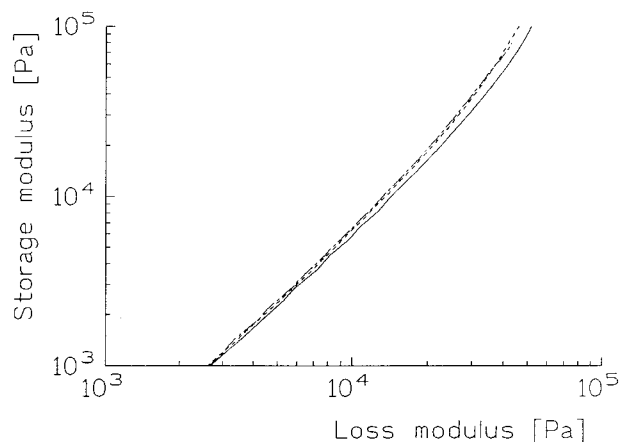
$$M_e = \rho RT/G_N^\circ \qquad (4)$$

where ρ is the density of the polymer, R is the gas constant and T the absolute temperature.

Table V   Values of Densities at 20°C and at Reference Temperature of the SAN Copolymers and of the Homopolymers

Reference	$\rho_{20°C}$	T_r (°C)	ρ_{T_r}
SAN95	1.046	187.6	0.980
SAN85	1.059	191.1	0.993
SAN75	1.072	194.6	1.007
PS	1.040	181	0.975
PAN	1.170		

Figure 7 Storage modulus versus loss modulus for SAN copolymers (—.—, SAN95; - - -, SAN85; —, SAN75).

In the case of the SAN copolymers, the densities of the melt at reference temperatures were estimated from those at 20°C and from values of the thermal expansion coefficients[24] for the homopolymers PS and PAN. The different values of densities are given in Table V.

Table IV summarizes the obtained values of the molecular weight between entanglements M_e. Because of its relation with the rubbery plateau modulus, the entanglement spacing M_e is influenced by the chemical composition of the SAN copolymers.

Han and Kim[25] have studied the influence of the composition for binary blends of poly(methyl metacrylate) and poly(vinylidene) and binary blends of poly(methyl metacrylate) and poly(styrene-co-acrylonitrile) on the evolution of log G' versus log G'' in the terminal zone. In our case, we used random copolymers instead of blends of polymers, and the influence of the composition is not well pronounced as shown in Figure 7.

CONCLUSION

The viscoelastic behavior in the melt of SAN copolymers was investigated by dynamic mechanical spectroscopy to point out the influence of the chemical structure. For comparison purposes it was necessary to estimate the influence of the acrylonitrile content on the free volume which requires the determination of the glass transition temperature. Differential scanning calorimetry analysis showed that the glass transition temperature changes with the acrylonitrile content of the copolymer. Thus, the comparison of the flow

curves has to be performed at the same $T - T_g$ temperature difference.

The Newtonian viscosity is influenced by the chemical composition of the SAN copolymers where the molecular weight distribution has only a secondary effect. The plateau modulus is also influenced by the acrylonitrile content; the plateau value was determined either at the middle of the width of the distance between two successive intersections of the storage and the loss moduli or as the value of the storage modulus G' at the minimum of the loss factor. The two ways of determination give approximately the same result.

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