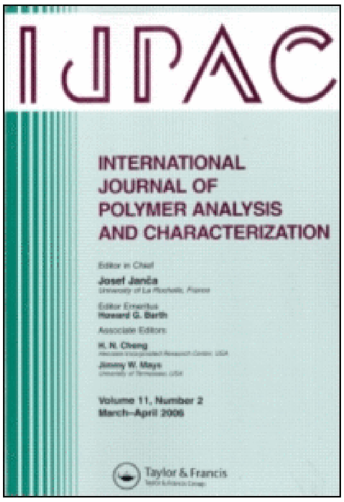

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Rheological Characterization of Styrene Methyl Methacrylate Copolymers

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The influence of copolymer composition on the rheological properties of random copolymers of styrene with methyl methacrylate (SMMA) obtained by radical polymerization in bulk was investigated. Differential scanning calorimetry (DSC) analysis shows that the glass-transition temperature of the copolymers increases with the methyl methacrylate (MMA) content. The knowledge of the glass transition is used to compare the different copolymers in an iso-free volume condition for melt rheology. Time temperature superposition was used to get a large frequency window ranging from the terminal zone up to the glassy plateau. The mechanical spectroscopy especially, was used to estimate the rubbery plateau modulus and the Newtonian viscosity. It has been possible to estimate the rubbery plateau modulus of SMMA copolymers from the experimental values of the corresponding homopolymers. For this particular system, the molecular weight between entanglement was shown to follow a simple blending law.

Keywords: SMMA copolymers; Rheological behavior; Rubbery plateau modulus

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In the past few years, rheology of polymers melts has been assessed as a reliable tool for polymer characterization. Especially, the molecular weight distribution (MWD) of linear polymer can be obtained from mechanical spectroscopy in the terminal zone, provided that a limited number of characteristic parameters of the polymer is known. These are mainly the plateau modulus, molecular weight between entanglement and the scaling law for the zero shear viscosity. Though these values are now well known for an increasing number of homopolymers, there is a lack of information concerning possible blending laws that could help to calculate these parameters for random or alternate copolymers.

The purpose of this article is to understand the influence of the composition and the molecular weight distribution of styrene-methyl methacrylate (SMMA) copolymers on rheological characteristics and particularly on the rubbery plateau modulus and the zero shear viscosity.

Additional interest would result if such work could lead to a general theory that enables the calculation of the parameters knowing only the chemical composition and structure of the monomer unit. Finally, if these blending laws prove to be valid they can be used to extrapolate the data for copolymers that are difficult to characterize by melt rheology (polyacrylonitrile, for example) because of their susceptibility to oxidation or hydrolysis or to processing. This work is a part of a project to understand these relationships.

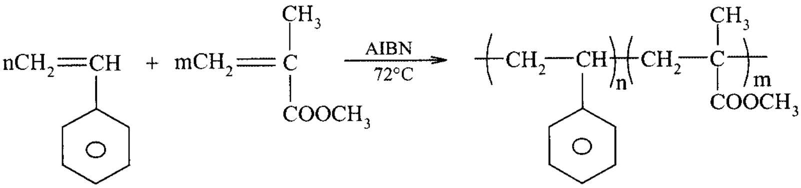
For the purpose of this study, SMMA copolymers were synthesized. These copolymers are interesting since they are expected to be random copolymers [1–4], because of the following reactivity ratio at 60°C: $r_{st} = 0.52$ and $r_{MMA} = 0.46$ [5]. To compare the different SMMA in an iso-free volume or iso-segmental friction factor condition, the rheological behavior must be considered at an iso-(T–T_g) temperature, and a study of the glass transition of the copolymers has been performed by means of the differential scanning calorimetry analysis.

Finally, the dynamic mechanical spectroscopy was used to characterize the material.

EXPERIMENTAL

Synthesis and Characterization

Styrene and methyl methacrylate (MMA) monomers were obtained from Acros Society and purified by distillation at reduced pressure. Radical-initiated bulk polymerization of styrene with methyl methacrylate was carried out in the presence of 2,2′ azobisisobutyronitrile (AIBN:2wt%) at 72°C with agitation for 14 h. The polymeric products



SCHEME 1

were purified after dissolving in butanone and precipitation in methanol (volume ratio butanone/methanol: 1/10) and dried in vacuum at 70°C. The yields of the copolymerization were close to 90%. Homopolymers (polystyrene and polymethyl methacrylate) were synthesized using the same conditions (see Scheme 1).

^{1}HNMR spectra have been recorded using a Brucker DRX 400 (400 MHz) spectrometer with chloroform-d ($CDCl_3$) as solvent. The compositions for different monomer feed ratios were determined by ^{1}HNMR and are given in Table I. These results were obtained by comparison between the aromatic and CH_3OCO protons signals that appear at different chemical shifts. The chemical shifts at 6.7–7.3 ppm and 3.6 ppm are respectively assigned to the aromatic group of styrene and to the CH_3OCO of methyl methacrylate.

Considering a chain with *n* styrene units and *m* methyl methacrylate units, the styrene content can be obtained with the ratio of the area signal at 6.7–7.3 ppm and of the peak at 3.6 ppm.

TABLE I Physical and chemical properties of the SMMA copolymers and of homopolymers.

Sample	Styrene content in the feed [wt %]	Styrene content in the copolymer by ^{1}HNMR [wt %]	M_w [g/mol]	I_p	M_n [g/mol]
SMMA1090	10	12.3	315000	2.8	113000
SMMA3070	30	33.8	307000	2.6	118000
SMMA6535	65	67.7	295000	2.4	121000
SMMA9010	90	89	235000	2.3	102000
PS			236000	2.2	105000
PMMA			318000	2.9	110000

$$\text{Molar \% styrene} = \frac{5n}{3m} = \frac{\text{area of aromatic signal}}{\text{area of CH}_3\text{ signal}} \tag{1}$$

with

$$n + m = 1 \tag{2}$$

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

$$w\%\ \text{styrene} = \frac{n\mathrm{M}_{\mathrm{st}}}{n\mathrm{M}_{\mathrm{st}} + m\mathrm{M}_{\mathrm{MMA}}} \tag{3}$$

where M_{st} = molar mass of monomer styrene, 104 g/mol and $\mathrm{M}_{\mathrm{MMA}}$ = molar mass of monomer methyl methacrylate, 100 g/mol.

Size exclusion chromatography (SEC) was performed using a Waters 150 CV system including a differential refractive index detector; ultra-Styragel columns (linear porosity 50 to 100,000 Å) and THF as the eluent were used. Monodisperse polystyrene standards allowed the determination of the calibration curve. Values of average molecular weights and polydispersity indices are summarized in Table I. It is worth noting that the molecular weight and the polydispersity index of the copolymers lie approximately in the same range.

Differential Scanning Calorimetry Analysis

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

Oscillatory Shear Flow

The samples of SMMA copolymers and homopolymers were compression molded at $T_g + 50°\mathrm{C}$ to process disks of 25 mm diameter and 1 mm thickness. They were stored in a vacuum oven at 60°C.

Rheological measurements in the melt were obtained in the 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 $T_g + 20°\mathrm{C}$ to high temperature in the frequency range 0.01 to 500 $\mathrm{rad.s}^{-1}$. Testing conditions were chosen in such a way that the observed behavior strictly obeys the law of linear viscoelasticity.

RESULTS AND DISCUSSION

Glass Transition

Figure 1 shows the thermogram of the styrene methyl methacrylate copolymers and of polystyrene (PS) and poly(methyl methacrylate) (PMMA). As expected, the glass-transition temperature of copolymers is between those of the homopolymers [1] and its unicity shows the random structure of the copolymers. In addition, T_g is sensitive to the level of methyl methacrylate in the copolymer and increases as the MMA content increases [1,6] (Table II). The increase of the glass transition is more pronounced at a high level of MMA. This finding is consistent with the observations of Ahuja [7] and Tordjeman et al. [1]. They attributed this result to the existence of intramolecular and intermolecular polar interactions between the ester groups, which are mainly responsible for the peculiar glass-transition behavior of PMMA[8–9].

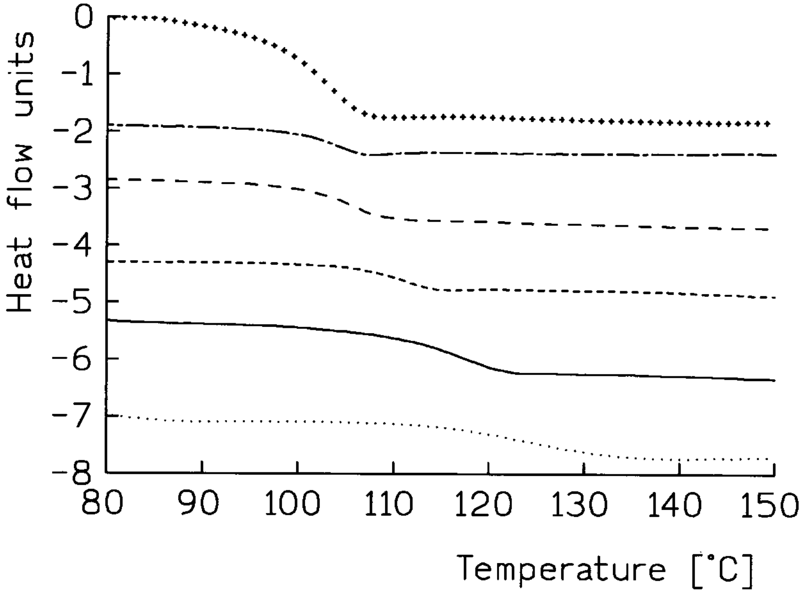


FIGURE 1 Thermograms for SMMA copolymers and homopolymers (—SMMA1090, – – –SMMA3070, — — —SMMA6535, –·–SMMA9010, . . .PMMA, +++ PS).

TABLE II Glass-transition temperature T_g and reference temperature T_r of the SMMA copolymers and of homopolymers.

Reference	T_g [°C]	T_r [°C]
SMMA1090	117.7	187.7
SMMA3070	111.1	181.1
SMMA6535	105.6	175.6
SMMA9010	104	174
PS	102.8	172.8
PMMA	122.5	192.5

Shift Factors and Time-Temperature Superposition

Measurements in oscillatory shear flow in the melt were performed at different temperatures ranging from $T_g + 20°C$ to high temperature. The determination of shift factors for time temperature superposition on each sample was carried out to obtain master curves at a reference temperature that varies with the MMA content in copolymers. The reference temperature T_r was chosen in order 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 SMMA copolymers, which proves the validity of the method for a comparison of the samples.

Because of the difference of the glass-transition temperature and the single curve of the shift factor, it is relevant to compare the rheological behavior in the melt of the samples at different reference temperatures. This is a necessary condition to obtain the iso-free volume condition. The understanding of the influence of the various structural parameters can be carried out only from such comparisons.

Zero Shear 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 is performed with T_r–T_g equal to 70°C.

The zero shear viscosities η_0 at the corresponding reference temperature are given in Table III. Despite the fact that SMMA1090, SMMA3070 and SMMA6535 have molecular weight distribution, that are rather identical, the zero shear viscosity is much higher for SMMA1090. This rheological parameter is influenced by the composition and increases with methyl methacrylate content. This should normally be reflected in the level of the plateau modulus, which is not susceptible to the MWD of the polymer.

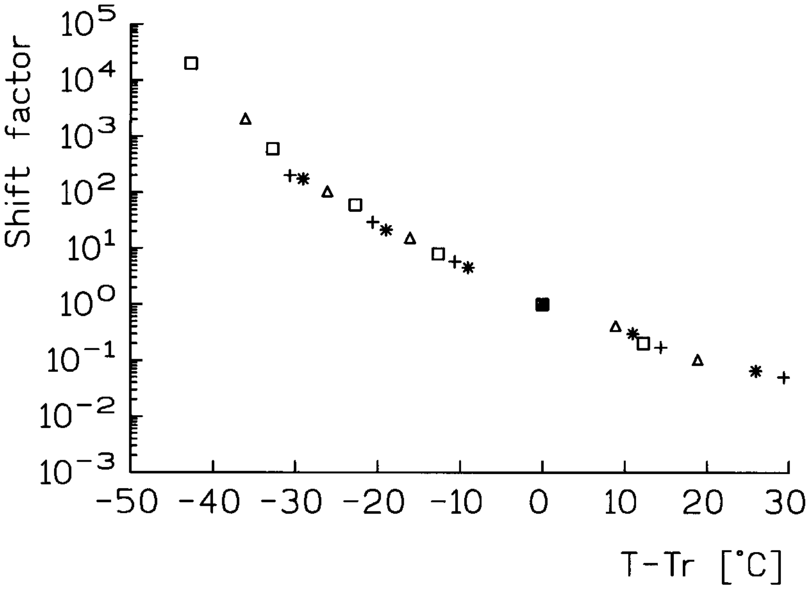


FIGURE 2 Shift factors for SAN copolymers (□ SMMA1090, △ SMMA3070, + SMMA6535, *SMMA9010).

Plateau Modulus

The rubbery plateau modulus G^0_N has been 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 a large plateau zone.

Though the value of this plateau seems to be influenced by the composition of the copolymer, and it is higher when the MMA 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 can be found in the literature to obtain an accurate value of the plateau.

For example, Marin proposed to determine G^0_N 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 SMMA and homopolymers are given in Table IV. As an example, Figure 5 shows the storage and the loss moduli for SMMA3070 and the various crossing points.

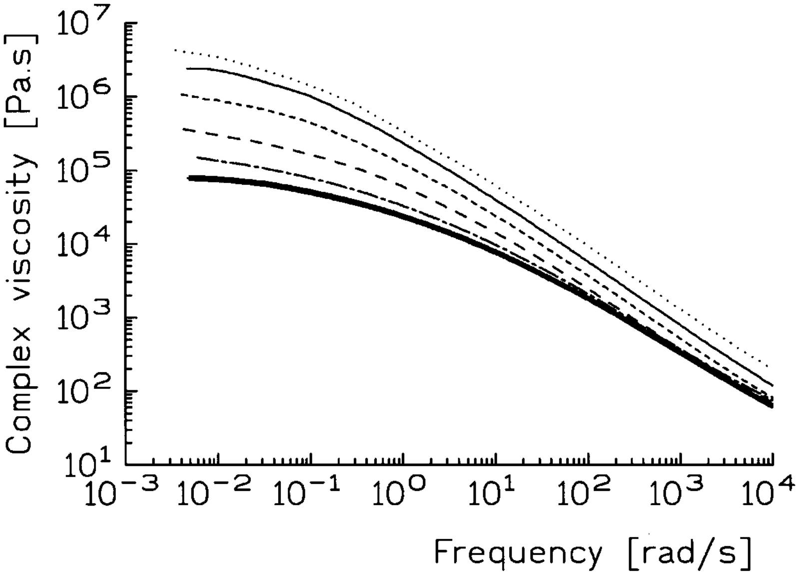


FIGURE 3 Complex dynamic viscosity for SMMA copolymers and homopolymers at T_r such that T_r–T_g = 70°C (—SMMA1090, - - -SMMA3070, — — —SMMA6535, –·–SMMA9010, ...PMMA, +++ PS).

Alternatively, some authors [11–14] have proposed that the value of the storage modulus G' at the minimum of the loss factor tanδ in the plateau zone may be a simple and reliable way to estimate G^0_N. The evolution of tanδ for SMMA3070 is given in figure 5. 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 results, the difference ranging between 2.5 and 7.4%.

TABLE III Zero shear viscosity of the SMMA copolymers and of homopolymers at T_r, such that T_r–T_g = 70°C.

Reference	η_0 [Pa.s]
SMMA1090	238×10^4
SMMA3070	106×10^4
SMMA6535	36.4×10^4
SMMA9010	14.9×10^4
PS	7.8×10^4
PMMA	421×10^4

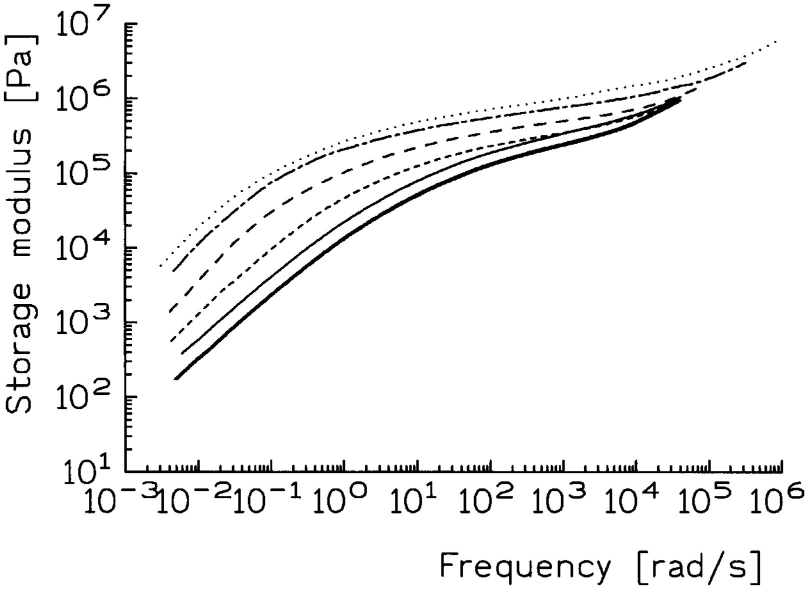


FIGURE 4 Storage modulus for SMMA copolymers and homopolymers at T_r such that $T_r - T_g = 70°C$ (—SMMA1090, - - -SMMA3070, — — —SMMA6535, –·–SMMA9010, …PMMA, +++ PS).

Different values of the rubbery plateau for PS and for PMMA are found in the literature.

- For PS: 0.2 MPa [10], 0.17 MPa [15,16] or 0.13 MPa [17,18]. The value 0.17 MPa is consistent with the value obtained for our PS.
- For PMMA: 0.66 MPa [1], 0.58 to 0.76 MPa[19]. The value obtained for our PMMA is consistent with the reference literature.

From the plateau modulus, it is possible to determine the molecular weight between entanglement M_e through the well-known equation derived from the kinetic theory of rubber elasticity [20].

$$M_e = \rho \mathrm{RT}/G_N^0 \tag{4}$$

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

In the case of the SMMA copolymers, the densities of the melt at reference temperatures were estimated from those at 20°C and from values of the thermal expansion coefficients [21] for the homopolymers polystyrene and poly(methyl methacrylate). The different values of

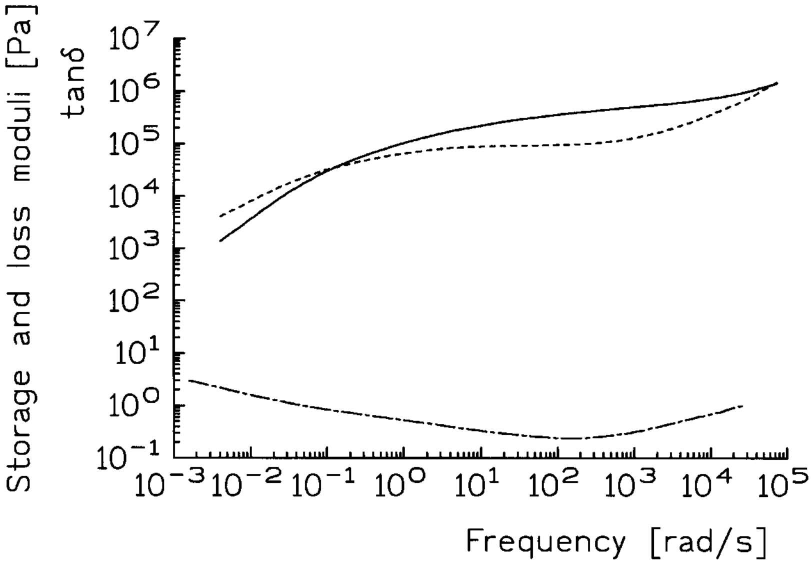


FIGURE 5 Storage and loss moduli and tanδ for SMMA3070 at T_r such that T_r–T_g = 70°C (– – –G', ———G'', – · –tanδ).

densities are given in Table V, and Table IV summarizes the 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 SMMA copolymers.

TABLE IV Rubbery plateau modulus and molecular weight between entanglements of the SMMA copolymers and of homopolymers.

Reference	G_N^0 [MPa] in the middle of $G'G''$ intersections	G_N^0 [MPa] at the minimum of tanδ	Relative difference [%]	M_e [g/mol] from G_N^0 in the middle of $G'G''$ intersections	M_e [g/mol] from G_N^0 at the minimum of tanδ
SMMA1090	0.555	0.569	2.5	7630	7450
SMMA3070	0.357	0.379	6.2	11400	10800
SMMA6535	0.230	0.247	7.4	16700	15600
SMMA9010	0.195	0.206	5.6	19100	18100
PS	0.170	0.182	7.0	21500	20100
PMMA	0.720	0.680	5.9	6040	6400

TABLE V Values of densities at 20°C and at reference temperature of the SMMA copolymers and of the homopolymers.

Reference	$\rho_{20^\circ C}$	T_r [°C]	ρ_{Tr}
SMMA1090	1.172	187.7	1.106
SMMA3070	1.139	181.1	1.080
SMMA6535	1.088	175.6	1.032
SMMA9010	1.056	174	1.001
PS	1.040	172.8	0.985
PMMA	1.190	192.5	1.124

Blending Law for the Molecular Weight Between Entanglements

Figure 6 shows a plot of the molecular weight between entanglement of the various SMMA copolymers as a function of their composition. From these data points, the molecular weight of the random copolymers obviously follows a simple linear blending law:

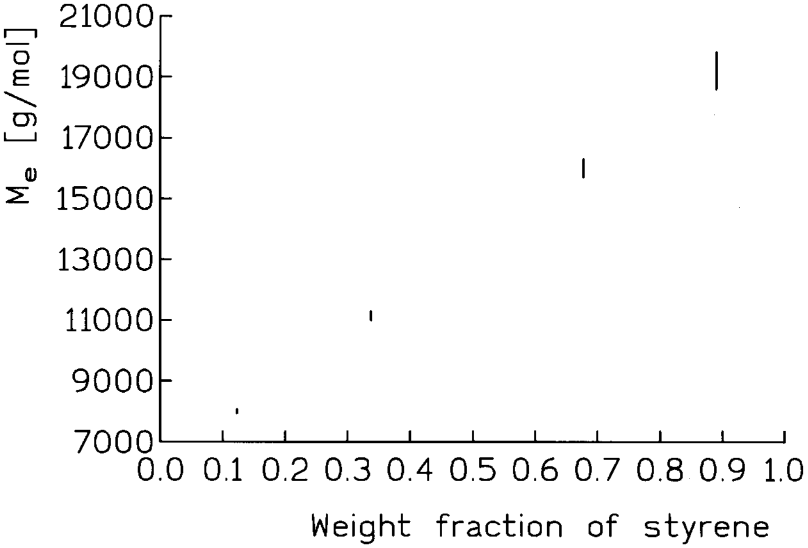


FIGURE 6 Molecular weight between entanglement versus composition for SMMA copolymers.

$$M_{e(\text{SMMA})} = \omega_{\text{PS}} M_{\text{PS}} + \omega_{\text{PMMA}} M_{\text{PMMA}} \tag{5}$$

ω_{PS} being the weight fraction of styrene monomer in the copolymer. Using this simple equation a maximum error of 8.6% was obtained when recalculating the values of G_N^0 for the various copolymers.

CONCLUSION

The viscoelastic behavior in the melt of random styrene methyl methacrylate copolymers was investigated by dynamic mechanical spectroscopy in order to point out the influence of the chemical structure. For this purpose, various SMMA copolymers were synthesized in the bulk using AIBN as an initiator. Similar MWD having polydispersity index of 2.2 to 2.9 were obtained for the materials. For comparison purposes it was necessary to estimate the influence of the MMA 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 MMA content of the copolymer. Thus, the comparison of the flow curves has to be performed at the same T–T_g temperature difference.

Because of the similarity of the polydispersity index the difference in the zero shear viscosity of the samples can be attributed to the chemical composition of the SMMA copolymers.

The plateau modulus is also found to be influenced by the MMA content; it 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. The molecular weight between entanglement was shown to follow a simple linear blending law.

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