Effects of molecular structure and composition on rheological behaviour of (methylmethacrylate *N*-phenylmaleimide) copolymers

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Abstract

The effects of different molecular weight distribution of (methylmethacrylate *N*-phenylmaleimide) copolymers of various molecular weights and their blends on the melt flow index, the storage and loss modulus, and the zero shear viscosity are investigated. Copolymers with higher *N*-phenylmaleimide contents and definite molecular structure show a typical thermal stability shown by their rheological properties. These studies seem to be useful for first estimations in screening tests and production control. © 1998 Elsevier Science Ltd. All rights reserved.

1. Introduction

There is considerable interest not only in the synthesis of new types of plastic materials, but also in the modification of the primary structure of existing polymers. The molecular structure of polymers is influenced in the radical copolymerization by the type of comonomers, the incorporated amounts of these comonomers and the distribution of the individual macromolecules. Differences in the primary structure affect conformational changes shown in their physical properties so that processing and application characteristics are influenced. The comonomer acrylonitrile improves the mechanical properties of styrene(S)/acrylonitrile(AN)-copolymers, especially the stiffness and toughness, in comparison to homopolystyrene [1]. Copolymerization of methylmethacrylate (MMA) with a monomer such as *N*-phenylmaleimide (NPI), whose five-membered planar ring completely hinders the rotation of the imide residues around the backbone chain of the macromolecule, leads to copolymers with great structural stiffness as well as a higher thermal stability [2]. As a consequence, the rheological properties vary with the content of NPI in the MMA/NPI-copolymer. Another way of modifying copolymers is by changing their molecular weights and molecular weight distributions. The influences of these parameters for many homo- and copolymers on their rheological properties are well known [3–13]. A better understanding of the relationship between these molecular parameters and rheological properties is very important from the standpoints of both polymer preparation and polymer processing.

The main objectives of the present study consist of two principal aspects: to investigate the influence of the composition of copolymers on their rheological properties; and to determine the effects of molecular weight and molecular weight distribution on rheological properties.

2. Investigated materials

- Free radical solution polymerizations of MMA and NPI were performed with the radical initiator azobisisobutyronitrile (AIBN) in 75 ml dioxane at 60°C in a discontinuous reactor. The total monomer concentration was maintained at 2.4 mol/l with 1.7 mol/l MMA and 0.7 mol/l NPI. The initiator concentration from the begin of the polymerization varies from 0.007 to 0.292 mol/l and addition of 15 ml of 0.226 mol/l to 0.406 mol/l AIBN after 60 min of the polymerization with start concentrations of 0.027 mol/l AIBN were performed. After the *in-situ* polymerization for a given time, the contents were poured into a large amount of methanol to precipitate the polymer. The polymer was filtered and purified by reprecipitation from methanol, and dried under reduced pressure for 24 h [14].

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- Compatible blends of the prepared copolymers were produced by mixing exact calculated amounts of copolymers (total 2 g) of similar compositions in 40 ml dichloromethane, followed by precipitation in a large amount of methanol. Recovery was carried out in the same way as described above. The obtained copolymers give bimodal molecular weight distributions [14].

The compositions of the used copolymers were determined if necessary by nitrogen analysis. Otherwise the similar glass transition temperatures indicate similar copolymer compositions, because of the increasing glass transition temperatures with higher NPI-content [2]. The parameters of molecular weight distribution were determined from the results of g.p.c. measurements on a WATERS 150CV chromatograph carried out with mixed columns at 35°C with THF as eluent and evaluated by means of relative calibration method based on polymethylmethacrylate (PMMA) standards.

3. Effects of molecular weight and molecular weight distribution

The traditional melt flow index (MFI) reflects the molecular weight and molecular weight distributions as well as the particular nature of intermolecular contacts between polymer molecules [4]. Especially the latter shows entanglements in the usual sense. In most polymeric melts, the viscosity is independent of shear rate at sufficiently low shear rates. The zero shear viscosity η_0 of linear polymers is proportional to the molecular weight below a critical value M_c, whereas above M_c it increases rapidly and becomes proportional to $M_w^{3.4}$:

$$\eta_0 = \begin{cases} K'M_w, & M_w < M_c \\ K'M_w^{3.4}, & M_w > M_c \end{cases} \tag{1}$$

The equation has been experimentally colaborated by many investigators [1,6–8,11,13]. The influence of molecular weight distributions on M_c is controversially discussed [7,15,16]. It is known that the moduli of polymers decrease with increasing molecular weight [9]. Therefore, the so-called cross-points of the storage and loss moduli [6] and the loss factors [5,10] depend on the molecular weight and even the molecular weight distribution.

3.1. Melt flow index (MFI)

The MFI was determined according to an international standard method (DIN 53735) using a Custom Scientific Instruments Melt Index Apparatus Model CS-127 MF (CSI) at 230°C with a load of 3.8 kg. The data for the materials which were used to determine the influences of molecular weight and/or molecular weight distribution with their MFI are summarized in Table 1. The correlation between MFI and weight average molecular weight shows

a proportionality (see Fig. 1). It is possible that the short chains act as a solvent in the samples which have bimodal molecular weight distributions. This phenomenon is marked by large deviations from the linear behaviour in low molecular weight samples. Above the critical entanglement molecular weight, linear polymers develops a network. Above $M_w = 120\,000$ g/mol, MMA/NPI-copolymers show no dependence on variations in molecular weight distributions, because of the complete development of the network. The MFI is above this molecular weight independent of the total chain length of the copolymer.

3.2. Storage and loss moduli

The dynamic moduli G′ and G″ were determined using Rheometrics Dynamic Analyzer RDA II (Rheometrics) in a frequency range between 0.0625 and 62.8 rad/s or 0.025 and 6.26 rad/s at four temperatures with a start temperature depending on the copolymers. Tables 1 and 2 summarize important data for all copolymers examined using the rheometer.

The crossover parameters ω_{c1} (and ω_{c2} at higher frequencies) were obtained according to the following equation:

$$G'(\omega_c) = G''(\omega_c) = G_c \tag{2}$$

It depends on the frequency range whether there are one, two or no cross-points. Fig. 2 illustrates a decrease of the critical frequency ω_{c1} with increasing molecular weight. With increasing molecular weight, the elastic properties of the MMA/NPI-copolymer predominate in the low-frequency region. The influence of molecular weight distribution on the second cross-point is summarized in Table 3. Increasing the polydispersity causes the shifting of ω_{c2} to lower frequencies. Higher polydispersities show an increasing of the elastic properties of the whole copolymer caused by more longer copolymer chains. As a consequence, the relaxation increases likewise. Analogous trends are also found in ω_{c1}, although the deviations for polydispersity of 2 to 3 cannot be denied.

3.3. The loss factor

According to Ferry [10], the frequency at which the minimum of the loss factor occurs depends on the molecular weight. Fig. 3 shows the shifting of the minimum of the loss factor with increasing molecular weight to lower frequencies and lower values. On the other hand, the minimum of the loss factor is shifted with increasing polydispersity towards lower frequencies and higher values (see Fig. 4). In addition, copolymers with higher polydispersity show at higher frequencies a characteristic maximum; the storage and loss factors have at this point the greatest distance. A comparison of the loss factors of copolymers with $M_w = 60\,000$–$70\,000$ g/mol gives similar results, although the values for the loss factor are higher.

Table 1
Samples of (MMA/NPI)-copolymers ordered with increasing M_w

Sample	M_w (g/mol)	M_n (g/mol)	M_w/M_n	Tg (°C)	$MFI_{230/3.8}$	η_0 205°C (P)	Ea (J/mol)
P1	61.000	33.000	1.9	173	2.93	n.a	n.a.
P2	61.500	29.700	2.1	169	3.50	1.09E + 06	3.56E + 05
P3	63.000	19.600	3.2	165	6.62	*1.72E + 06*	2.37E + 05
P4	63.200	29.900	2.1	153		5.41E + 06	n.a.
P5	63.200	18.200	3.5	168		3.28E + 06	2.24E + 05
P6	63.300	17.800	3.6	159	5.63	n.a.	2.94E + 05
P7	63.600	22.800	2.8	146		n.a.	n.a.
P8	64.300	11.100	5.8	161	8.48	3.28E + 06	2.37E + 05
P9	67.300	12.500	5.4	169	14.88	n.a.	1.89E + 05
P10	68.800	25.500	2.7	172	3.41	n.a.	n.a.
P11	70.000	22.600	3.1	153		n.a.	n.a.
P12	74.800	26.800	2.8	155		n.a.	n.a.
P13	89.600	35.100	2.6	172	1.31	6.29E + 06	2.90E + 05
P14	90.600	36.200	2.5	173	0.89	1.14E + 07	2.96E + 05
P15	93.200	42.800	2.2	154		2.63E + 06	2.63E + 05
P16	93.400	37.700	2.5	154		4.11E + 06	2.24E + 05
P17	94.200	19.100	4.9	168	3.35	3.03E + 07	1.77E + 05
P18	94.400	39.700	2.4	171		5.31E + 06	3.28E + 05
P19	97.700	40.600	2.4	155		1.89E + 06	2.51E + 05
P20	102.900	26.600	3.9	168	2.51	3.64E + 07	2.03E + 05
P21	105.700	15.200	7.0	166	5.97	n.a.	1.61E + 05
P22	111.000	46.000	2.4	165		9.38E + 06	2.71E + 06
P23	120.300	25.800	4.7	165		1.27E + 08	1.94E + 05
P24	120.800	15.300	7.9	163	2.78	n.a.	n.a.
P25	123.400	43.600	2.8	168	1.05	n.a.	n.a.
P26	124.700	57.600	2.0	153	1.20	n.a.	n.a.
P27	127.600	33.900	3.8	171	1.83	9.64E + 06	2.17E + 05
P28	132.200	29.600	4.5	166	1.56	n.a.	n.a.
P29	133.000	66.900	2.0	161		6.15E + 06	2.65E + 05
P30	135.300	49.300	2.7	191		3.06E + 06	2.86E + 05
P31	142.800	50.400	2.8	171		*5.35E + 06*	1.84E + 05
P32	167.500	87.300	1.9	154		1.21E + 07	1.21E + 05
P33	244.300	78.200	3.1	168		*3.87E + 07*	2.19E + 05
P34	271.900	127.200	2.1	162		4.15E + 07	2.80E + 05

n.a.: not available
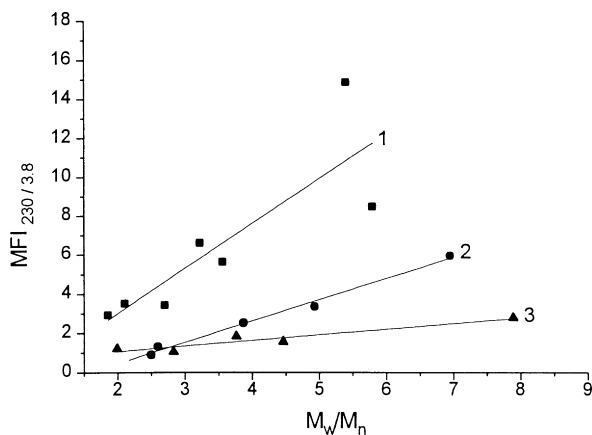Italic type: extrapolated from the activation energy

Fig. 1. Melt flow index MFI as a function of polydispersity M_w/M_n for different values of M_w (1, $M_w \approx 60\,000$–$70\,000$ g/mol; 2, $M_w \approx 90\,000$–$100\,000$ g/mol; 3, $M_w \approx 120\,000$–$130\,000$ g/mol) samples—see Table 1.

3.4. Zero shear viscosity

For all polymers, the data extends to low enough frequencies so that the zero shear viscosity attains a constant value of η_0:

$$\eta_0 = \lim_{\omega \to 0} |\eta^*(\omega)| \tag{3}$$

The zero shear viscosity could not be reached for several samples in the frequency range investigated. In this case, the zero shear viscosities were extrapolated from the activation

Table 2
Samples of (MMA/NPI)-copolymers with similar M_w/M_n and crossover parameters

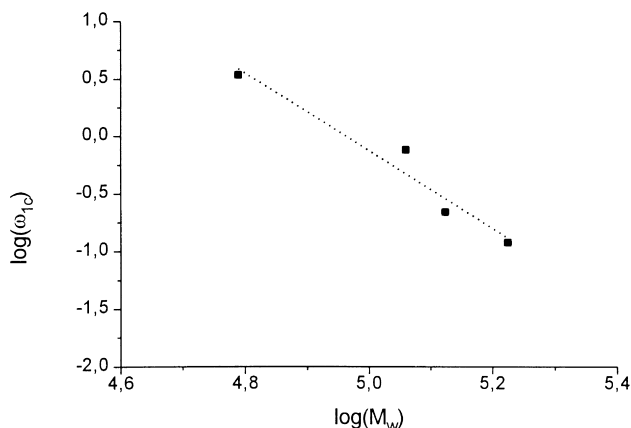| Sample	M_w (g/mol)	M_w/M_n	ω_{c1} 205°C (rad/s)	G_{c1} 205°C (dyn/cm^2)
P2	61.500	2.1	3.42	4.33E + 05
P26	114.700	2.0	0.76	5.51E + 05
P29	133.000	1.9	0.22	2.41E + 05
P32	167.500	2.1	0.12	3.25E + 05

Fig. 2. Critical frequency ω_{1c} as a function of the molecular weight M_w with $M_w/M_n \approx 2.0$ (P2, P26, P29, P32) ($T = 205°C$).

energy and the a_T shift using the following formula which is valid for low temperature differences.

$$a_T = \frac{\eta_0(T)}{\eta_0(T_0)} = \exp\left[-\frac{Ea}{R}\left(\frac{1}{T} - \frac{1}{T_0} \right) \right] \qquad (4)$$

Fig. 5 compares the zero shear viscosities for two polydispersities. No influence of the polydispersity is proved for the investigated copolymers. As a consequence, the constants of Eq. (1) show only slight deviations (see Table 4).

The well-known 3.4 power dependence at high molecular weights was not found. The molecular weight range, which starts from $M_w = 61\,500$ g/mol, is most probably above the critical molecular weight for MMA/NPI-copolymers. The critical molecular weight for PMMA is in the value range of 27 500–31 200 g/mol [10,17]. Calculations of the critical molecular weight for MMA/NPI-copolymers from the minimum of loss factor (tanδ) as given by the following equation [8,10]

$$\tan\delta_{\min} = 1.15\left(\frac{M_w}{M_c} \right) \qquad (5)$$

gives a range limit of 30 000–70 000 g/mol. An exact determination is not possible because of the strict validity of Eq. (5) for monodisperse homopolymers [10]. A reduction of chain lengths caused by the experiment temperature analogous to that of the S/AN-copolymers investigated by Sandner [1] was taken into account. A comparison of the molecular weight distributions, before and after the measurements with the rheometer, as obtained by the g.p.c., points out that the influence of temperature could be neglected. The use of M_z or M_n according to Saeda [7]

Table 3
Influence of M_w/M_n of the second cross-point

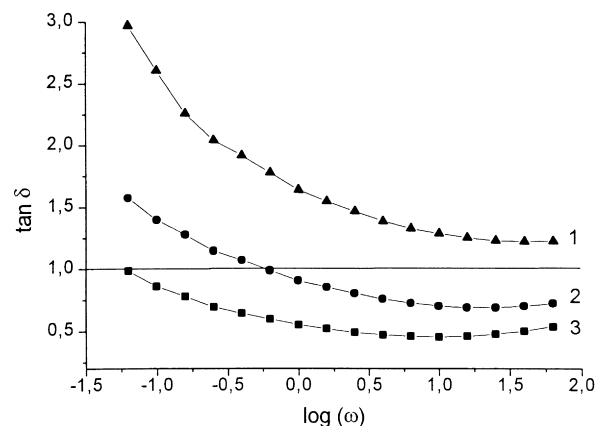| Sample	M_w/M_n	$\omega_{c2}\ T = 205°C$	$\omega_{c2}\ T = 210°C$
P18	2.4	43.63	
P14	2.5	19.67	47.09
P13	2.6	19.17	31.61
P17	4.9	8.79	14.99

Fig. 3. Loss factor tanδ as a function of the frequency ω for different molecular weights M_w with $M_w/M_n \approx 3.0$ (1, $M_w = 63\,000$ g/mol; 2, $M_w = 142\,800$ g/mol; 3, $M_w = 244\,300$ g/mol) (P3, P31, P33) ($T = 215°C$).

gives higher slopes of 2.6 or 2.7 for a sample with a polydispersity of 2.0. An approach to the 3.4 power which requires data from a remarkably wide range of linear polymers could not be investigated. According to Vinogradov and Malkin [18], the slopes decrease below 3.4 caused by the presence of short chains, which could be the case for a sample with a polydispersity of 3.0. In these cases, empirical equations using M_n and M_w including a great number of constants for homologous polymer series could be approximated. According to Halary [8], the $\eta_0 - M_w$-relation is not influenced by the polydispersity. Low differences in the molecular weight influence the $\eta_0 - M_w/M_n$-relation, and low values of M_w of MMA/NPI-copolymers from 60 000–70 000 g/mol confirm Halary's observation, in contrast to higher values of molecular weight (see Fig. 6). The steady shear viscosity increases with polydispersity at higher molecular weights. The reason for this is that the short polymer chains could act as a solvent for long chains, so that the difference in zero shear viscosity is negligible at low molecular weights.
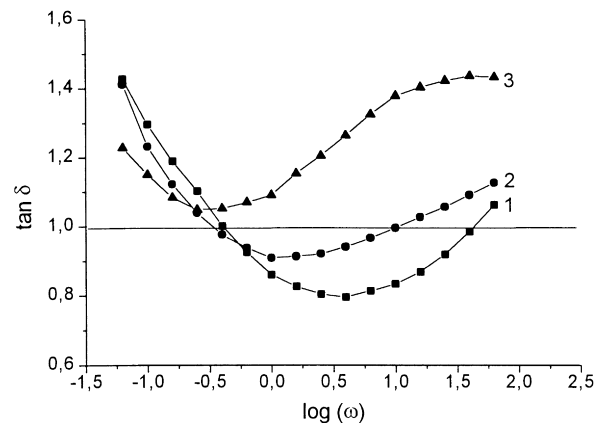

Fig. 4. Loss factor tanδ as a function of the frequency ω for different polydispersity M_w/M_n with $M_w \approx 100\,000$ g/mol (1, $M_w/M_n = 2.4$; 2, $M_w/M_n = 4.9$; 3, $M_w/M_n = 7.0$) (P18, P17, P21) ($T = 205°C$).
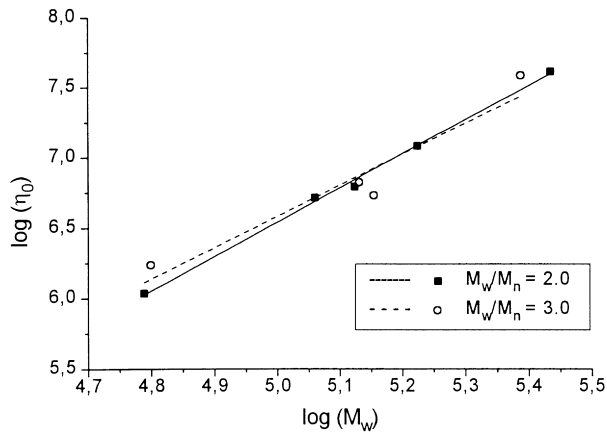
Fig. 5. Zero shear viscosity η_0 as a function of the molecular weight M_w samples—see Table 1 ($T = 205°C$).

Table 4
Comparison of the constants of Eq. (1)

M_w/M_n	Constant K'	Exponent
2.0	2.19×10^{-6}	2.4
3.0	2.51×10^{-6}	2.2

4. Effects of copolymer composition on rheological behaviour

The copolymer composition affects the rheological quantities. Changes caused by the molecular weight or molecular weight distribution were eliminated using MMA/NPI-copolymers with constant molecular weight and polydispersity (2.0 and 3.0).

4.1. Storage and loss moduli

Comparison of the storage and loss moduli shows changes with respect to compositions of MMA/NPI-copolymers (see
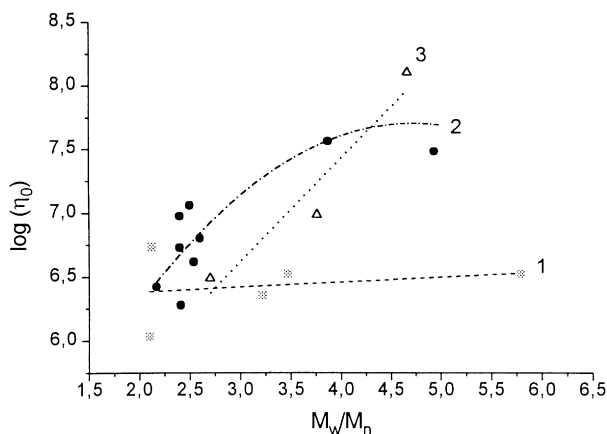

Fig. 6. Zero shear viscosity η_0 as a function of the polydispersity M_w/M_n (1, $M_w \approx 60\,000–70\,000$ g/mol; 2, $M_w \approx 90\,000–100\,000$ g/mol; 3, $M_w \approx 120\,000–130\,000$ g/mol) samples—see Table 1 ($T = 205°C$).
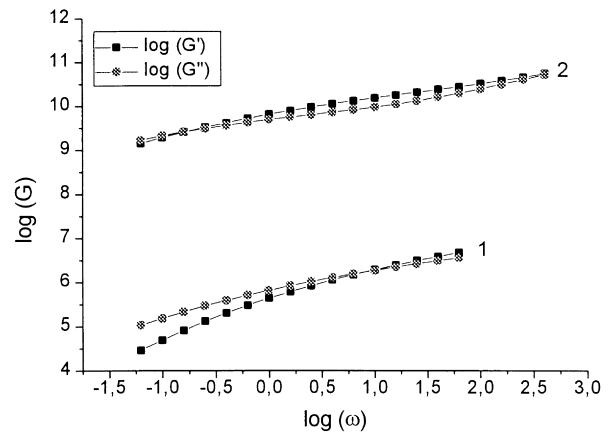

Fig. 7. Comparison of loss- and storage moduli for different copolymer compositions (1, 25.2 mol% NPI_P; 2, 34.6 mol% NPI_P) (P31, P35, P36) ($T = 235°C$).

Fig. 7). The lower the content of NPI in the copolymer the lower are the values for the moduli. The two moduli are strongly dependent on frequency. Copolymers with higher NPI-contents attain the plateau modulus already in the low-frequency region. The plateau region starts at increasingly lower frequency as the content of NPI is increased. Similar trends have been reported for the response of S/AN-copolymers [1]. The transition region in which the change from the rubbery state to the glassy state begins, occurs in this low-frequency region. This leads to the known elevation of stiffness of copolymers with higher NPI-content. As a consequence, the critical frequencies of the cross-points decrease with increasing content of NPI in the copolymer.

4.2. The loss factor

The loss factor as a quotient of loss to storage moduli is likewise dependent on the copolymer composition (see Fig. 8). The minimum of the loss factor is with higher content of NPI in the copolymer shifted to lower frequencies. The greater stiffness of the copolymer caused by the higher NPI-content is indicated by the plane minimum of the loss factor. The time dependence of the loss factor is not so clearly divided into viscous and elastic regions. The minimum of the loss factor shifts with higher content of NPI in the copolymer to lower frequencies. The material is less viscous, in contrast to the copolymers with lower contents of NPI.

4.3. Zero shear viscosity

In addition to two MMA/NPI-copolymers with about $M_w = 145\,000$ g/mol (P31, P35) and 25.2 and 34.6 NPI_P (mol%) a copolymer (P36) with $M_w = 90\,100$ g/mol and 44.7 NPI_P (mol%) was taken into consideration. The zero shear viscosity was determined using the common Eq. (3) (P31: $\eta_0 = 1.42E + 06$ P and P35: $\eta_0 = 1.17E + 07$ P). The zero shear viscosities were extrapolated, if necessary (P36:
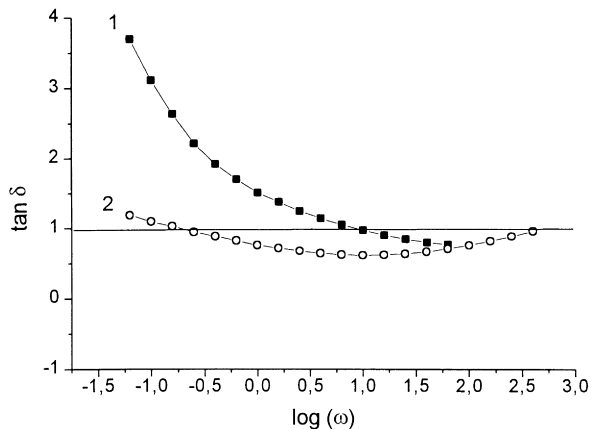
Fig. 8. Loss factor tanδ as a function of the frequency ω for different copolymer compositions (1, 25.2 mol% NPI$_P$; 2, 34.6 mol% NPI$_P$) (P31, P35) ($T = 235°C$).
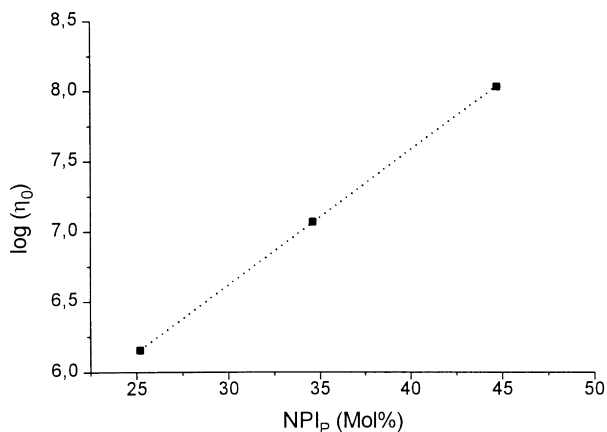

Fig. 9. Zero shear viscosity as a function of copolymer composition (P31, P35, P36) ($T = 235°C$).

$\eta_0 = 1.08E + 06$ P). The elevation of the zero shear viscosities is proportional to the NPI-content in the MMA/NPI-copolymer (see Fig. 9). The results are similar to observations on the AN-content in S/AN-copolymers [1]. The zero shear viscosity shows no diminution caused by the lower molecular weight of the sample. The differences in the molecular weights are low enough so that there is no influence on the zero shear viscosities.

5. Conclusions

By analyzing rheological data obtained on MMA/NPI-copolymers, generalized relationships describing the influences of molecular weight and molecular weight distributions have been found and confirmed.

- The MFI is above $M_w = 90\,000$ g/mol dependent on changes of molecular weight distributions.
- The critical frequencies ω_{1c} and ω_{2c} decreases with increasing molecular weight and polydispersity, because

of the increasing elasticity of the whole copolymer with longer polymer chains.
- The minimum of the loss factor shifts to lower frequencies with increasing molecular weight and polydispersity; the values of the loss factor increase with increasing M_w, but decrease with increasing polydispersity. The molecular reasons are the same described for the critical frequencies.
- The zero shear viscosity is proportional to the molecular weight. The exponent of the dependence of zero shear viscosity on M_w is determined to be 2.2–2.4, which is lower than the literature value of 3.4. The zero shear viscosity is increased through great differences in molecular weight distributions. The influence of the NPI-content in the MMA/NPI-copolymers show comparable trends to the results found for AN in S/AN-copolymers.
- The lower the content of NPI in the copolymer the lower are the values of the loss and storage moduli.
- Copolymers with higher NPI-content attain the plateau modulus already in the low-frequency region.

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