A critical analysis of the models connecting molecular mass distribution and shear viscosity functions

L. Macskási*

Scientific Society of Mechanical Engineering, Fő utca 68, H-1027 Budapest, Hungary

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Abstract. Thermoplastics having various short and long-chain branches, characterized by the melt index measured at the processing temperature – according to their average molecular mass – can be processed using universal principles, independently of their chemical composition. The average molecular mass is the result of a molecular mass distribution, being the fingerprint of the chemical synthetic technology. The actual shape of the shear viscosity function aiming at the quantitative characterization of viscous flow, containing material-dependent parameters, depends on the ratio of high and low molecular mass fractions, the width of the molecular mass distribution function and on the number of short and long chain branches. This publication deals with the critical analysis of the mathematical methods of transforming these two curves of basic importance into each other.

Keywords: rheology, molecular mass, molecular mass distribution, shear viscosity function, direct and indirect transformation model

1. Introduction

1.1. Establishing a research hypothesis

Table 1 shows the stations of the technical-scientific quest during which a plastic product is made by cooling and shaping a melt produced by melting a polymer mass in the plastics processing industry. There are three separate, well-defined research areas: polymer structure research, testing the viscous flow properties of polymer melts, and testing the processing properties. First two are mainly scientific disciplines, the third is a practice-oriented activity. Our main interest was in establishing mutual relations between them, taking into account especially the works of Bersted [1–3], Malkin and Teishev [4–6], Tuminello and coworkers [7, 8] and Nobile et al. [9], who dealt first with determining the molecular mass distribution functions of thermoplastics from melt viscosity functions.

2. Experimental

2.1. Materials

The materials used in our experiments were

- polystyrenes of Edistir type (Dunasytr Plc, Hungary), samples denoted as PS 1-11
- PVC pellets of various K-values of Ongrolit type, (BorsodChem Plc, Hungary), samples denoted as PVC 1-6
- polypropylene homopolymers of Tipplen type (TVK Plc, Hungary), samples denoted as PP 1-6

The samples are listed in Table 2.

2.2. Test methods

2.2.1. Determining the molecular mass distribution by GPC

The molecular mass of polymers influences their general performance, such as tensile strength, elas-

*Corresponding author, e-mail: macskasi.levente@chello.hu
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Table 1. Research hypothesis

A	Polymers	AB/BA	B	Polymer melts	BC	C	Processing properties		
Molecular mass distribution	Mutual correspondence between polymer structure and macroscopically measurable flow properties		Flow curve	Determining melt elasticity (rheological swelling) from shear flow data		Extrusion	Exit pressure		
Molecular mass			Shear viscosity function				Rheological swelling		
Short chain branching			Normal stress curve				Elastic turbulence (melt fracture)		
Long chain branching			Normal viscosity function			Injection molding	Internal pressure in the mold		
Structural studies			Rheological tests			Rheological swelling	Yes	No	
Gel permeation chromatography			Capillary viscometer			Processing method	Extrusion	Injection molding	
X-ray diffraction			Rotation viscometer			Molecular mass	Medium and high	Low and medium	
Infrared spectroscopy			Extrusion meter			Molecular mass distribution	Wide	Medium	
			Injection mold with built-in sensors			Temperature	Low and medium	High	
			Extensional rheometer			Production rate	Low and medium	High	

Table 2. Carreau parameters obtained by fitting the rheological test results of the polymers studied at 190°C by Equation (6) and the molecular mass distribution constants of Equation (1) obtained from the GPC data

Polymer	Carreau parameters				GPC test data				Parameters of the molecular mass distribution curve		
	η_0 [Pa·s]	λ [s]	M	N	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$	M_{max}	α	σ	μ
EDISTIR polystyrene											
PS-1	23451	0.930	0.771	0.773	162634	64072	2.538	132359	0.026503	0.6305	4.9559
PS-2	18131	0.774	0.760	0.749	157532	58431	2.696	124360	0.026422	0.6860	4.9116
PS-3	11762	0.580	0.983	0.553	160375	62151	2.580	150795	0.026831	0.6444	4.9172
PS-4	43449	1.433	0.891	0.713	176472	71525	2.467	138452	0.027770	0.5758	5.0266
PS-5	23955	0.951	0.825	0.711	189487	88165	2.149	160388	0.025332	0.5200	5.0492
PS-6	48157	2.208	0.777	0.779	158968	58993	2.695	128254	0.023147	0.7882	4.9204
PS-7	41720	1.369	0.763	0.816	131583	59117	2.226	102684	0.028333	0.6216	4.9437
PS-8	13197	0.551	0.873	0.677	150708	55342	2.723	124857	0.027397	0.6978	4.9101
PS-9	61515	2.673	0.865	0.701	187972	95438	2.873	151415	0.027990	0.7419	4.9958
PS-10	39817	1.564	0.816	0.768	150680	55797	2.701	112421	0.026919	0.5917	5.0165
PS-11	77149	4.110	0.714	0.842	150798	53184	2.835	124135	0.029322	0.5970	5.1160
ONGROLIT PVC											
PVC-1 (K=52)	1432	0.861	0.426	0.362	80035	40049	1.998	68941	0.02585	0.5212	4.7364
PVC-2 (K=58)	7824	0.782	0.725	0.575	106986	52384	2.042	89182	0.02634	0.5292	4.8465
PVC-3 (K=64)	19759	0.481	0.988	0.586	145541	68544	2.123	119524	0.02768	0.5722	4.9804
PVC-4 (K=67)	32531	0.636	1.027	0.603	164508	80261	2.050	133922	0.02742	0.5160	5.0522
PVC-5 (K=70)	50453	0.677	1.445	0.483	188065	87418	2.151	160780	0.02919	0.5509	5.1185
PVC-6 (K=77)	167418	0.855	1.028	0.923	253923	114367	2.220	192797	0.02822	0.5481	5.2508
TIPPLEN polypropylene											
PP-1	1491	0.076	0.845	0.679	212850	45274	4.701	110710	0.05481	0.8058	4.9795
PP-2	1470	0.066	0.901	0.672	219166	46200	4.744	118050	0.05740	0.7840	4.9762
PP-3	7479	0.448	0.724	0.791	269912	55980	4.822	158117	0.04550	0.7828	4.9858
PP-4	11009	0.706	0.912	0.618	336073	68097	4.935	188315	0.04519	0.8634	5.1434
PP-5	61349	2.826	1.288	0.468	480786	89048	5.399	319716	0.03139	0.8710	5.1959
PP-6	69067	1.821	1.067	0.570	617606	107993	5.719	526621	0.03371	0.9653	5.3282

ticity modulus, while their molecular mass distribution plays a decisive role in their processing.

In order to determine the molecular mass distribution the polymer is usually dissolved and the so-called size-exclusion chromatogram (or gel permeation chromatogram, GPC) is determined. The are no

known solvents for certain polymers (e.g. poly(tetrafluorethylene), poly(ether-ether-ketone)), while other can be studied only at high temperature (polyolefins). Solvent based techniques are usually time consuming not because of the GPC test itself, but because of the dissolution of the polymer sample.

Solutions of about 5 mg/ml concentration were made from PS in tetrahydrofurane and from PVC in cyclohexanone at room temperature, while solutions of about 0.5–1 mg/ml concentration were made from PP in 1,2,4-trichlorobenzene at 160°C, which were filtered on filters with 1 µm pore diameter. Molecular mass distribution curves of PS and PVC samples were measured at room temperature using a *Waters* gel permeation chromatograph (GPC), while the molecular mass distribution of PP samples was determined by a Polymer Laboratories GPC 220 equipment at 160°C. Polystyrene standards were used for calibration in each case.

2.2.2. Determining the shear viscosity function

Modern rheological test equipments (oscillating rheometers and capillary or rotation viscometers) make possible determining the frequency dependence of storage and loss moduli or the flow curves within 20 minutes and 1–2 hours respectively, covering 4 orders of magnitude frequency range or 6–8 orders of magnitude shear rate range respectively. They need neither solvent nor filtering. Therefore, rheological tests are ideally suited for quality control.

Mass and volume flows of the melts were measured using standard capillaries at 190°C, using 1–21.6 kg load. Shear stress, shear rate and shear viscosity values were calculated from the test data.

3. Quantitative description of the molecular mass distribution and critical analysis of determining their maximum shear viscosity

3.1. Mathematical description of the molecular mass distribution determined by GPC method

Characteristic parameters of the distribution curve are determined by the GPC test software, namely the mass- and number average molecular masses and the molecular mass belonging to the maximum of the distribution function.

Mass average molecular mass of the polymers studied was in the range of $100\,000 < \bar{M}_m < 600\,000$ their polydispersity was moderate ($2 < \bar{M}_m/\bar{M}_n < 6$). The functional form, i.e. the differential molecular mass distribution was described by the so-called log-normal distribution (Equation (1)):

$$y = \frac{a}{\sigma} \exp \left[-\frac{1}{2} \frac{\ln x - \mu}{\sigma^2} \right] \quad (1)$$

which is strictly valid only for linear, monodisperse polymers, mainly for polyethylene [10], but can be used as a good approximation for commercial polymers (e.g. for polypropylene, polystyrene, and PVC samples [11]), provided that they do not contain too many branches and if the polydispersity is not too large. a is a constant characterizing the maximum of the curve, σ is the standard deviation of the distribution, x is the molecular mass, μ is the molecular mass belonging to the maximum of the curve. Using the constants of Equation (1) the polydispersity index of the polymer is given by Equation (2):

$$\frac{\bar{M}_m}{\bar{M}_n} = 1 + \left(\frac{\sigma}{\mu} \right)^2 \quad (2)$$

3.2. Critical analysis of the determination of the maximum shear viscosity

The shear viscosity function of polymer melts can be determined by a combined use of rotational and capillary rheometers in a broad shear rate range. Viscosity values close to the zero shear rate can be obtained by the former, while viscosities closer to the values encountered in practice can be obtained by the latter. Depending on the polymer and on the temperature it is possible to measure points at low shear rates ($\sim 0.1 \text{ s}^{-1}$) by capillary rheometers, but these are not typical.

The functional relation is usually described by functions containing 2, 3 or 4 parameters, resulting in gradually smaller fitting errors. Equations with 2 parameters cannot handle the Newtonian behavior, which can be described only by equations containing 3–4 parameters. One has to interpret the physical meaning of the parameters and the reality of the maximum viscosity value obtained.

The problem of determining the η_0 values lies in the fact that test data are determined in the so-called non-Newtonian range, and the usual, simpler extrapolation methods do not treat this range adequately.

When describing the shear viscosity as a function of the shear rate by Equation (3):

$$\eta = \frac{1}{a_1 \dot{\gamma} + b_1} \quad (3)$$

and linearization $b_1 = 1/\eta_0$ is yielded by the intercept.

Describing the shear viscosity by another function, namely Equation (4):

$$\eta = \frac{(\eta_0)_2}{\dot{\gamma}^{a_2}} \tag{4}$$

After linearization the shear viscosity belonging to $\dot{\gamma} = 1 \text{ s}^{-1}$ is the intercept, i.e. $(\ln \eta_0)_2$ and the shear viscosity increases monotonously and continuously with decreasing shear rates which is physically impossible.

When using a three-parameter Equation (5):

$$\eta = \frac{(\eta_0)_3}{(\dot{\gamma} + b_3)^{a_3}} \tag{5}$$

the horizontal section characteristic of the Newtonian range, i.e. the maximum shear viscosity appears in the logarithmic plot, but parameters a_3 and b_3 have no physical meaning.

The Carreau equation originally containing 3 parameters [12] has been modified to contain 4 parameters (see Equation (6)):

$$\eta = \frac{(\eta_0)_4}{[1 + (b_4 \dot{\gamma})^{c_4}]^{a_4}} \tag{6}$$

which contains not only the maximum shear viscosity (η_0) but also the relaxation time ($b_4 = \lambda$), as a material constant, a value (c_4) characterizing the molecular mass distribution and a further parameter (a_4) characterizing the non-Newtonian behavior can also be determined from it.

Figure 1 shows the curves fitted to shear viscosity data measured on PS-4 at 190°C. We concluded, that at low shear rates Equation (4), while at high shear rates Equation (3) leads to erroneous conclu-

Figure 1. Determining the maximum shear viscosity of sample PS-4 by approximate equations at 190°C

sions, reflected by the relatively large fitting errors (18.06 and 9.13% respectively). Equations (5) and (6) can be well applied in the whole shear rate range, the fitting errors are only 2.38 and 2.15% respectively.

Carreau parameters of PS, PVC and PP samples determined form 190°C rheological tests are collected in Table 2 together with the parameters of the molecular mass distribution functions determined by GPC.

3.3. Relation between the maximum shear viscosity and the mass average molecular mass

3.3.1. Literature data

Calculation the maximum shear viscosity is of great theoretical importance, as it is directly related to the mass average molecular mass of the polymer, as shown by Equation (7) [13–15]:

$$\eta_0 = K_1 \cdot \overline{M}_m^\alpha \tag{7}$$

Parameters collected from the literature for HDPE, PS and PP are listed in Table 3. It has to be noted that K_1 parameters were obtained using zero shear viscosities using Poise units.

Figure 2 shows the relations between shear viscosities and mass average molecular masses for our PS,

Table 3. The constants of Equation (7) for various polymers at 190°C

	Polymer	K_1	α	R^2	Reference
Literature data	HDPE	–12.700	3.5200		[16]
	PS	–12.800	3.4000		[17]
	PP	–11.900	3.6900		[18]
Calculated from test data	PS	–32.545	7.0823	0.9964	
	PP	–17.099	3.8211	0.9475	
	PVC	–16.207	3.9698	0.9881

Figure 2. Maximum shear viscosities determined at 190°C plotted against the molecular mass

PP and PVC samples. Zero shear viscosities are given here already in SI units.

The molecular mass range of the PS samples studied covers a very narrow range and, according to Equation (7) the slope is about double of the value obtained from the literature.

The exponent calculated for the polystyrene sample is too high, therefore the calculated molecular masses are far from the GPC results. The reason for this discrepancy is that the shear rate which can be realized in the capillary viscometer is not low enough to obtain a reliable zero shear viscosity by processing the data using the Carreau equation. There are two further methods which, however, require special instrument. Zero shear viscosity can be determined by oscillating rheometry. A third method uses the slope of the steady state of the deformation curve determined by creep experiments at low stresses.

4. A model used for transforming molecular mass distribution curves into shear viscosity functions

4.1. Theory

When establishing the relation between the polymer structure and macroscopically observed properties we started from the obvious fact that shear viscosity depends mainly of the chain length distribution, on the temperature and last, but not least on the shear rate [19, 20].

Bersted in his works [1–3] defined a critical molecular mass M_c , below which the molecular flow is regarded as Newtonian, while above this value the viscosity decreases with the shear rate. The critical molecular mass is essentially related to the Newtonian/non-Newtonian transition in the flow curve, which in its turn is related to the maximum relaxation time. Consequently the onset of the non-Newtonian flow is related to the longest relaxation time of the polymer sample.

Stated otherwise it is assumed that for each shear rate there exists a M_c critical molecular mass. If $M < M_c$ the weight of contribution of molecules to the viscosity is proportional to $w_i M_i$, while if $M \geq M_c$ the contribution is proportional to their weight fraction, as if their molecular mass were M_c . It is further assumed that the threshold value is independent of the average molecular mass of the

sample and of the molecular mass distribution of the whole sample.

4.2. Calculation method

In order to determine the critical molecular mass we start from the well known Equation (4) between maximum shear viscosity (η_0) and mass average molecular mass $\bar{M}_m$ as described in linearized form by Equation (8):

$$\lg \eta(\dot{\gamma}) = K_1 + \alpha \cdot \lg \bar{M}_m \quad (8)$$

where Equation (9) defines the meaning of $\bar{M}_m$:

$$\bar{M}_m = \sum_{i=1}^{c-1} w_i M_i + M_c \sum_{i=c}^{\infty} w_i \quad (9)$$

where w_i is the mass fraction of the i -th component and M_i is the molecular mass of the i -th component. The molecular mass distribution curve has been divided into $i = 54$ discrete points (see Figure 3). Rheological constants of the studied polymer types were determined from the shear viscosities measured at 190°C using the Carreau equation (see Equation (10)):

$$\eta = \frac{\eta_0}{[1 + (\lambda \cdot \dot{\gamma})^M]^N} \quad (10)$$

wherein η_0 is the maximum shear viscosity in Pa·s units; λ is the relaxation time [sec]; M is a dimensionless constant characterizing the molecular mass distribution, while N is another dimensionless constant characterizing the non-Newtonian behavior. At a given shear rate the ‘apparent’ molecular masses are calculated from Equation (8), from which the M_c value is calculated using Equation (9).

Figure 3. Molecular mass distribution of sample PS-4. 1 – GPC data, 2 – the curve fitted by Equation (1)

Table 4. Calculation of critical molecular mass of sample PS-4

Shear rate [s ⁻¹]	Viscosity [Pa·s]	Molecular mass	M _c Critical molecular mass								
			i = 30	i = 33	i = 34	i = 35	i = 36	i = 37	i = 38	i = 39	i = 40
1	18334	205458	307909	372962	403199	439192	482179	534168	597966	677532	777749
10	5921	147352	212793	249068	264817	282740	303060	326200	352689	383174	418180
20	4074	132004	187670	216343	228266	241415	255748	271268	287902	305423	323205
100	1690	101906	138401	152168	156587	160376	162967	163545	160853	152951	136955
1000	477	70237	86561	84643	81166	75106	65343	50198	27171	−7480	−59018
2000	326	62788	74367	68760	63426	55049	42381	23537	−4273	−45216	−105113
5000	197	54138	60209	50318	42827	31761	15718	−7420	−40783	−89033	−158636
10000	134	48396	50809	38074	29152	16300	−1983	−27972	−65023	−118122	−194170

Figure 4. Shear viscosity (η , in Pa·s units), molecular mass (M_m) and critical molecular mass (M_c) of sample PS-4 as a function the shear rate

When determining the M_c values it was observed that after a certain i value M_c becomes negative, which is physically meaningless. Therefore an $i = c$ value was adopted, where a positive M_c was obtained even at the highest shear rate, i.e. $i = 35$ (Table 4).

When plotting the logarithm of the M_c values against the logarithm of the shear rate a monotonically decreasing curve was obtained. Using the slope of the latter the following Equation (11) was used to calculate the M_c values:

$$M_c = M_{c,0} \cdot \dot{\gamma}^{-1/4} \tag{11}$$

where $M_{c,0} = 320\,000$ is used for PS [1]. A serious drawback of Equation (11) is that it approximates the measured shear viscosity function only in the non-Newtonian rage, but it cannot be used to calculate the Newtonian range. We tried to eliminate this deficiency first by a relation of $M_c = a/(\dot{\gamma} + b)$ but a good result was obtained only by using a relation of $M_c = A/[1 + (B \cdot \dot{\gamma})^C]^D$ (see Figure 4).

4.3. Results and discussion

The molecular mass distribution is transformed into the shear viscosity function in the following way:

- (1) knowing the average molecular mass and the molecular mass distribution curve of the polymer one calculates $A = M_c$ at zero shear rate using Equation (12):

$$A = M_{c(\dot{\gamma}=0)} = \frac{\overline{M}_m - \sum_{i=1}^{c-1} w_i M_i}{\sum_{i=c}^{\infty} w_i} \tag{12}$$

for an $i = c$ value as close as possible to the average molecular mass.

- (2) then the points of the shear viscosity function are calculated using Equation (13):

$$\eta = \exp \left\{ K_1 + \alpha \cdot \lg \left[\sum_{i=1}^{c-1} w_i M_i + \frac{A}{(B \cdot \dot{\gamma}^C + 1)^D} \cdot \sum_{i=c}^{\infty} w_i \right] \right\} \tag{13}$$

Table 5 summarizes the data obtained from the GPC curves of the PS, PVC and PP samples, the constants of the measured and calculated shear viscosity functions and their deviations. Relative differences, $\sum_i 100 \cdot [(\eta_{measured} - \eta_{calculated})/\eta_{measured}]$ are mostly within 10%.

5. Model used to determine molecular mass distribution of thermoplastic polymers from dimensionless rheological data

5.1. Theory

Having discussed the direct problem (i.e. the determination of the flow curve from a known molecular mass distribution) in Chapter 4 the following question is asked: is it possible to calculate the molecu-

Table 5. Parameters of the measured and calculated shear viscosity functions of the polymers tested and their relative differences

Polymer	GPC curve			Shear viscosity function (measured)				Shear viscosity function (calculated)				Rel. diff. [%]
	i = c	$\sum_{i=c}^{\infty} w_i$	$\sum_{i=1}^{c-1} w_i M_i$	η [Pa·s]	λ [s]	M [-]	N [-]	A	B	C	D	
EDISTIR polystyrene												
PS-1	36	0.2991	47019	23451	0.930	0.771	0.773	517979	0.2059	0.5658	0.8393	8.093
PS-2	34	0.3896	40387	18131	0.774	0.760	0.749	429558	0.2289	0.4765	0.9533	13.247
PS-3	34	0.3661	44471	11762	0.580	0.983	0.553	377485	0.1500	0.5198	1.0569	6.852
PS-4	35	0.3714	42342	43449	1.433	0.891	0.713	590576	0.3540	0.4137	1.0686	8.244
PS-5	29	0.4685	40725	23955	0.951	0.825	0.711	397664	0.2447	0.4614	1.0153	6.392
PS-6	34	0.4877	32162	48157	2.208	0.777	0.779	512694	0.4319	0.4058	0.9238	6.029
PS-7	36	0.2954	49504	41720	1.369	0.763	0.816	699714	0.2205	0.4054	1.4811	8.838
PS-8	34	0.3842	38520	13197	0.551	0.873	0.677	390846	0.1582	0.4974	1.0616	6.545
PS-9	34	0.4143	43666	61515	2.673	0.865	0.701	647189	0.3035	0.3638	1.4798	8.619
PS-10	36	0.3242	47493	39817	1.564	0.816	0.768	638157	0.2900	0.4514	1.1377	10.236
PS-11	26	0.3502	54752	77149	4.110	0.714	0.842	635773	0.2645	0.4005	1.4376	10.369
average								530694	0.2593	0.4510	1.1323	
ONGROLIT PVC												
PVC-1	38	0.1093	52452	1432	0.8613	0.4262	0.3618	210222	0.1614	0.3754	1.3456	1.905
PVC-2	32	0.3014	39808	7824	0.7817	0.7252	0.5751	253643	0.2355	0.5238	0.6539	4.033
PVC-3	29	0.4116	37204	19759	0.4814	0.9878	0.5859	265778	0.1747	0.6005	0.6584	5.677
PVC-4	28	0.4598	36431	32531	0.6361	1.0273	0.6028	285609	0.6165	0.5507	0.7320	6.480
PVC-5	27	0.4941	35451	50453	0.6770	1.4448	0.4833	303241	0.1922	0.8042	0.4917	9.247
PVC-6	24	0.6382	25541	167418	0.8545	1.0281	0.9231	360242	0.2748	0.5590	0.8721	11.649
average								279789	0.2759	0.5689	0.7923	
TIPPLEN polypropylene												
PP-1	32	0.2207	71954	1491	0.0762	0.8454	0.6795	591533	0.04397	0.6027	1.0503	4.206
PP-2	32	0.2271	71143	1470	0.0655	0.9006	0.6720	574811	0.03294	0.6099	1.2131	4.708
PP-3	34	0.2010	112249	7479	0.4478	0.7236	0.7911	980237	0.03764	0.5296	1.3421	2.860
PP-4	31	0.3464	79132	11009	0.7061	0.9115	0.6180	768597	0.19658	0.4688	0.9415	6.047
PP-5	31	0.4442	87236	61349	2.8264	1.2884	0.4681	1066568	0.30630	0.3872	1.1782	11.270
PP-6	30	0.4604	112572	69067	1.8207	1.0668	0.5705	988648	0.23650	0.4343	1.2560	9.704
average								828399	0.14230	0.5054	1.1635	

lar mass distribution from the shear viscosity function? This so-called ‘inverse problem’ is regarded as ‘ill-defined’ by Malkin and Teishev [4–6], Tuminello and coworkers [7, 8] and Nobile et al. [9]. Although molecular mass distribution curves calculated from low amplitude dynamic oscillation tests have been published in the literature, the algorithm has not been published [21, 22].

Typical industrial polymers are polydisperse, i.e. they can be regarded as mixtures of monodisperse fractions. Flow curves/shear viscosity functions of monodisperse polymer melts can be described by Equation (14):

$$\eta(\dot{\gamma}) = \begin{cases} \eta_0 & \text{if } \tau \leq \tau_s \text{ or } \dot{\gamma} \leq \dot{\gamma}_s \\ \frac{\tau_s}{\dot{\gamma}} & \text{if } \tau > \tau_s \text{ or } \dot{\gamma} > \dot{\gamma}_s \end{cases} \quad (14)$$

where η_0 is the maximum shear viscosity, τ_s the critical shear stress and $\dot{\gamma}_s = \tau_s/\eta_0$ is the critical

shear rate depending on the molecular mass of the high molecular mass fractions.

The molecular mass dependence of η_0 is given by Equation (7) wherein K and α are constants ($\alpha = 3.4\text{--}3.5$). The critical shear rate can be calculated by Equation (15):

$$\dot{\gamma}_s = \frac{\tau_s}{\eta_0(M)} = \frac{\tau_s}{KM^\alpha} \quad (15)$$

Equation (15) is strictly valid only for monodisperse polymers, for polydisperse samples mass average molecular mass $\bar{M}_m$ should be used. For a binary mixture of homodisperse polymers with M_1 and M_2 ($M_1 > M_2$) Friedman and Porter [23] introduced the following Equation (16):

$$\eta_{0,combination} = K\bar{M}_m^\alpha = (w_1\eta_{0,1}^{1/\alpha} + w_2\eta_{0,1}^{1/\alpha})^\alpha \quad (16)$$

where $\eta_{0,1}$ and $\eta_{0,2}$ are Newtonian viscosities and w_1, w_2 are the mass fractions of the components.

The flow curve/viscosity function of the binary mixture can be expressed by Equation (17):

$$\eta(\dot{\gamma}) = \begin{cases} K(w_1 M_1 + w_2 M_2)^\alpha & \text{if } \dot{\gamma} \leq \frac{\tau_s}{KM_1^\alpha} \\ \left[w_1 \left(\frac{\tau_s}{\dot{\gamma}} \right)^{1/\alpha} + w_2 K^{1/\alpha} M_2 \right]^\alpha & \text{if } \frac{\tau_s}{KM_1^\alpha} \leq \dot{\gamma} \leq \frac{\tau_s}{KM_2^\alpha} \\ \frac{\tau_s}{\dot{\gamma}} & \text{if } \dot{\gamma} \geq \frac{\tau_s}{KM_2^\alpha} \end{cases} \quad (17a)$$

$$\eta(\dot{\gamma}) = \begin{cases} \left[w_1 \left(\frac{\tau_s}{\dot{\gamma}} \right)^{1/\alpha} + w_2 K^{1/\alpha} M_2 \right]^\alpha & \text{if } \frac{\tau_s}{KM_1^\alpha} \leq \dot{\gamma} \leq \frac{\tau_s}{KM_2^\alpha} \end{cases} \quad (17b)$$

$$\frac{\tau_s}{\dot{\gamma}} \quad \text{if } \dot{\gamma} \geq \frac{\tau_s}{KM_2^\alpha} \quad (17c)$$

This approximation has been generalized by Nobile et al. [9] for a continuous molecular mass distribution as shown by Equation (18):

$$\eta(\dot{\gamma}) = \left[\int_0^{M(\dot{\gamma})} (KM^\alpha)^{1/\alpha} f(M) dM + \left(\frac{\tau_s}{\dot{\gamma}} \right)^{1/\alpha} \int_{M(\dot{\gamma})}^{\infty} f(M) dM \right]^\alpha \quad (18)$$

where $f(M)$ is the molecular mass distribution function.

The first member of Equation (18) corresponds to the second member of Equation (17b) while its second member corresponds to the first member of Equation (17b). The first member of Equation (18) represents the Newtonian flow, while its second member is related to those high molecular mass fractions, which take part in the non-Newtonian flow.

In order to solve the inverse problem three dimensionless variables are needed, namely

- dimensionless shear viscosity according to Equation (19):

$$Y = \left[\frac{\eta(\dot{\gamma})}{\eta_0} \right]^{1/\alpha} \quad (19)$$

- dimensionless shear rate according to Equation (20):

$$X = \left(\frac{\dot{\gamma}}{\dot{\gamma}_s} \right)^{1/\alpha} \quad (20)$$

- and dimensionless molecular mass according to Equation (21):

$$m = \frac{1}{X} = \frac{M}{M_m} \quad (21)$$

where the molar masses belonging to certain shear rates should be used instead of M , as shown by Equation (22):

$$M = \frac{10^{\frac{1}{\alpha}(\lg \eta_0 + K)}}{\left(\frac{\lambda \dot{\gamma}}{k} \right)^{1/\alpha}} \quad (22)$$

where η_0 is the maximum shear viscosity, K is a constant characterizing the polymer, λ is the relaxation time, $\dot{\gamma}$ is the actual shear rate and $k = 1$.

Without presenting the derivation the solution of the inverse problem is given by Equation (23):

$$f\left(\frac{1}{X}\right)_{\frac{1}{X}=m} = - \left(X^4 \frac{d^2 Y}{dX^2} + 2X^3 \frac{dY}{dX} \right) \quad (23)$$

5.2. Calculation of the molecular mass distribution

Equation (23) can be made appropriate for calculations if the Carreau equation modified by us is inserted into Equation (24):

$$Y = \frac{1}{[1 + (kX^\alpha)^M]^{N/\alpha}} \quad (24)$$

then it is derived twice with respect to X as shown in Equation (25):

$$\frac{d^2 Y}{dX^3} = MNk^M X^{\alpha M - 2} \cdot \frac{M(N + \alpha)k^M X^{\alpha M} - (\alpha M - 1)(1 + k^M X^{\alpha M})}{(1 + k^M X^{\alpha M})^{(N/\alpha + 2)}} \quad (25)$$

Using Equation (25) the frequency of each molecular mass in any polymer sample can be determined as a function of the shear rates used in the rheologi-

cal test if the Carreau constants (λ , M , N), and the constants of the given polymer (k and α) are known.

5.3. Results and discussion. Comparison of calculated and measured molecular mass distributions

GPC curves are usually taken at points equally distributed along the log (molecular mass) axis, therefore it would be useful to distribute uniformly the test points along a logarithmic scale for melt viscosity tests too. The latter is hampered by the fact that even with up-to-date capillary rheometers one can take 6–8 (10) test point pairs (depending on the conditions). Intermediate points in the measured shear rate interval can be estimated by interpolation using the fitted shear viscosity function. A major problem is that in the case of $\dot{\gamma} < 0.1 \text{ s}^{-1}$ test are impossible, or even if one can measure 1–2 points for low viscosity melts, the scatter of parallel points will be unacceptably high. The same is true for tests at $\dot{\gamma} > 100 \text{ s}^{-1}$ where short test times do not allow the establishment of stationary flow. Additionally one cannot maintain the constant test temperature because of fictional heating. Thus the shear viscosity function must be extrapolated above and below the tested interval in order to estimate the high and low molecular mass branches of the molecular mass distribution function.

We could not describe the breadth of the distribution using the algorithm developed for the indirect problem. For a long time the Carreau parameters were blamed for this failure, but without success. Later we concentrated on the effect of varying k and especially α which brought us closer to the solution of the problem.

The lack of success was due to the improper exponent value in equation $\eta_0 = K\bar{M}_m^\alpha$. We stuck too much to the $\alpha = 3.4$ regarded as universal in the literature which made impossible the approximately correct prediction of the molecular mass distribution. If a smaller α value is chosen, the lower (high molecular mass) and higher (low molecular mass) portions of the distribution function can be approximated with acceptable error. The irregular double peak still remains in the central range, which has been published in ref. [22] too.

The problem mentioned above is related to the accuracy of shear viscosity determination, which

can be illustrated by the $\ln \eta_0 - \bar{M}_m$ relation. The sensitivity of η_0 to the molecular mass at infinite shear rate is unity ($\alpha = 1.0$), while at zero shear viscosity it is much higher ($\alpha = 3.4$). At 190°C , depending on the polymer the lowest shear rate, from where extrapolation to zero shear viscosity is performed is $0.5\text{--}20 \text{ s}^{-1}$ therefore the empirically found values of $2 < \alpha \leq 3.4$ seem to be logical.

Figures 5–7 show the calculated and experimental molecular mass distribution curves (the latter are determined by GPC). The shape of the calculated curves deviates considerably from the experimental ones, and the mentioned anomaly appears on all of them. Serious discrepancies are found in the relative frequencies. In the case of the PVC-4 sample, however, a very good agreement was found.

$\bar{M}_m$, $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ values calculated from rheological tests and from the GPC are summarized in Table 6. It has been concluded that the model approximates well the original molecular mass distribution. Unfortunately the same cannot be said of mass and number average molecular masses. Both values are underestimated in most cases, the calcu-

Figure 5. Comparison of calculated ($\diamond$) and measured (GPC, $\blacksquare$) molecular mass distribution curves of sample PS-4

Figure 6. Comparison of calculated ($\diamond$) and measured (GPC, $\blacksquare$) molecular mass distribution curves of sample PVC-4

Table 6. Comparison of measured and calculated molecular mass distributions of polystyrene, PVC and polypropylene

Polymer type	Calculated from rheological tests (k = 1)				Obtained form GPC tests			Relative difference* [%]		
	α	M_m	M_n	M_w/M_n	M_m	M_n	M_w/M_n	M_m	M_n	M_w/M_n
EDISTIR polystyrene										
PS-1	2.50	73977	26623	2.779	162634	64072	2.538	−54.51	−58.45	9.48
PS-2	2.60	75399	29189	2.583	157532	58431	2.696	−52.14	−50.05	−4.19
PS-3	2.65	74803	29948	2.498	160375	62151	2.580	−53.36	−51.81	−3.19
PS-4	2.70	79243	32754	2.419	176472	71525	2.467	−55.10	−54.21	−1.93
PS-5	2.80	78929	34608	2.281	189487	88165	2.149	−58.35	60.75	6.13
PS-6	2.50	64685	23279	2.779	158968	58993	2.695	−59.31	−60.54	3.11
PS-7	2.85	83002	37403	2.219	131583	59117	2.226	−36.92	−36.73	−0.31
PS-8	2.50	77018	27718	2.779	150708	55342	2.723	−48.90	−49.92	2.04
PS-9	2.45	63067	21815	2.891	187972	65458	2.873	−66.45	−66.67	0.63
PS-10	2.55	71360	26662	2.676	150680	55797	2.701	−52.64	−52.22	−0.91
PS-11	2.50	57951	20856	2.779	150798	53184	2.835	−61.57	−60.79	−1.99
ONGROLIT PVC										
PVC-1	3.40	53566	28208	1.899	80035	40049	1.998	−33.07	−29.57	−4.96
PVC-2	2.80	77283	36622	2.110	106986	52384	2.042	−27.76	−30.09	3.34
PVC-3	2.55	91487	43707	2.093	145541	68544	2.123	−37.14	−36.24	−1.40
PVC-4	2.55	111655	53689	2.080	164508	80261	2.050	−32.13	−33.11	1.45
PVC-5	2.40	116814	53497	2.184	188065	87418	2.151	−37.89	−38.80	1.51
PVC-6	2.30	209115	100680	2.077	253923	114367	2.220	−17.65	−11.97	−6.44
TIPPLEN polypropylene										
PP-1	2.050	155261	34187	4.542	121850	45274	4.701	27.42	−24.49	−3.39
PP-2	2.025	166486	36659	4.541	219166	46200	4.744	−24.04	−20.65	−4.27
PP-3	1.975	116050	23800	4.876	269912	55980	4.822	−57.00	−57.48	1.12
PP-4	1.950	105580	20858	5.062	336073	68097	4.935	−68.58	−69.37	2.57
PP-5	1.900	95560	18162	5.262	480786	89048	5.399	−80.12	−79.60	−2.55
PP-6	1.875	122628	21480	5.709	617606	107993	5.719	−80.14	−80.11	−0.18

*relative difference = 100 · (calculated from rheological tests – obtained from GPC tests)/(obtained from GPC tests)

Figure 7. Comparison of calculated (♦) and measured (GPC, ■) molecular mass distribution curves of sample PP-3

lated values are about half – two third of the values obtained form the GPC tests.

5.4. Critical evaluation of the applicability of the model

Table 7. shows how the mass- and number average molecular masses and the distribution itself change with the maximum shear viscosity and with the relaxation time. The data reflect a positive feature of the model, namely

- number average molecular mass ($\bar{M}_n$) increases parallel with the maximum shear viscosity, i.e.

Table 7. Mass- and number average molecular masses and polydispersities obtained form them

As a function of the maximum viscosity ($\lambda = 1.0$ s, $M = 0.8$, $N = 0.7$)							
η_0 [Pa·s]	12500	15000	17500	20000	22500	25000	30000
M_m	105805	111634	116812	121491	125773	129732	136878
M_n	36283	38281	40057	41661	43130	44487	46938
M_m/M_n	2.916						
As a function of the relaxation time ($\eta_0 = 22500$ Pa·s, $M = 0.8$, $N = 0.7$)							
λ [s]	0.25	0.50	0.75	1.00	1.25	1.50	2.00
M_m	116771	122194	125498	125773	124263	122262	118476
M_n	50014	46234	44575	43130	41610	40196	37908
M_m/M_n	2.335	2.643	2.815	2.916	2.986	3.042	3.125

with the mass average molecular mass ($\bar{M}_n$), the distribution remains constant, if the relaxation time (λ) and the Carreau parameters (M and N) remain constant;

- the increase of the relaxation time (λ) results in the broadening of the distribution curve if the maximum shear viscosity (η_0), and the Carreau parameters (M and N) are kept constant.

A negative feature of the model is that by increasing the M parameter of the Carreau equation results in a gradually narrower distribution, i.e. the algorithm handles the breadth of the molecular mass distribution inversely.

6. Prediction of the molecular mass distribution of thermoplastics using a model based on the GEX function

6.1. Theory

The method described in Chapter 5. was based on the double derivation of the experimentally determined shear viscosity function. The integral molecular mass distribution function was obtained by processing the first and second derivatives using the described algorithm. Irregularities of the upper branch of the curve and the fact that by increasing the M parameter of the Carreau equation resulted in narrower distribution, i.e. that the algorithm handled the breadth of the molecular mass distribution inversely, prompted us to try the General Exponential (GEX) function, as suggested by Nobile et al. [9], to describe the molecular mass distribution function. It is to be noted, however, that only monomodal distributions with a single peak can be described by the GEX function, shown in Equation (26):

$$f_{GEX}(M; a, b, M_0) = \frac{b}{M_0 \Gamma\left(\frac{a+b}{b}\right)} \left(\frac{M}{M_0}\right)^a \cdot e^{-\left(\frac{M}{M_0}\right)^b} \quad (26)$$

where $\Gamma(x)$ is the gamma function, a and b are constants, M is the mass average molecular mass, M_0 is the reference molecular mass.

The starting point is again the experimentally determined shear viscosity function and the four parameters of the Carreau equation (η_0 , λ , M and N) fitted to the experimental points.

The rheological model is defined by a 5-parameter ($\eta_{0,GEX}$, K_{3GEX} , a_{GEX} , b_{GEX} and α_{GEX}) GEX function shown in Equation (28), derived from the assumed form of the molecular mass distribution function (see Equation (27)):

$$\left(\frac{\eta}{\eta_{0,GEX}}\right)^{1/\alpha} = \frac{\frac{K_3}{\dot{\gamma}^{1/\alpha}} \cdot \Gamma\left(\frac{a+1}{b}, \left[\frac{K_3}{\dot{\gamma}^{1/\alpha}}\right]^b\right) - \Gamma\left(\frac{a+2}{b}, \left[\frac{K_3}{\dot{\gamma}^{1/\alpha}}\right]^b\right)}{1 + \frac{\Gamma\left(\frac{a+2}{b}\right)}{\Gamma\left(\frac{a+1}{b}\right)}} \quad (27)$$

where $\Gamma(x, y)$ is the incomplete gamma function given by Equation (28):

$$\Gamma(x, y) = \Gamma(x) - \int_0^y t^{x-1} \cdot e^{-t} dt \quad (28)$$

and $a, b > 0$. Notations introduced by Nobile et al. [9] are used in the equations.

6.2. Calculation of the molecular mass distribution

The parameters are calculated by fitting Equation (27) to the experimental data using nonlinear regression method.

M_1 and M_0 molecular masses necessary for the further calculation are obtained knowing two further parameters – K_1 and K_2 – defined by Equations (29) and (30):

$$M_1 = \left(\frac{\eta_0}{K_1}\right)^{1/\alpha} \quad (29)$$

$$M_0 = \frac{1}{K_3 K_2^{1/\alpha}} \quad (30)$$

Molecular mass data of the distribution function are obtained according to Equation (22) where η_0 is the maximum shear viscosity, K is a polymer-specific constant, λ is the relaxation time, $\dot{\gamma}$ is the actual shear rate and $k = 1$. The corresponding $w(m)_{GEX}$ values are obtained from Equation (26). Of course these should be normalized according to the $\sum w_i m_i = 1$ relation.

The algorithm was tested with PS/PVC/PP samples and it turned out that the calculated distribution curves approximate best those obtained by GPC if $a < b$ and $K_1 = K_2 = 1-2.25$.

6.3. Results and discussion. Comparison of the calculated and measured molecular mass distribution

Figures 8–10 show the molecular mass distribution curves obtained by the GPC method and calculated from shear viscosity function for one PS, PVC a PP sample.

Table 8 presents the constants calculated by the GEX-model for the polymers included in this study, $\overline{M}_m$, $\overline{M}_n$ and $\overline{M}_m/\overline{M}_n$ values, which are compared with those obtained from the GPC tests. Both molecular mass and the distribution values exhibit (with some exceptions) less than 30% deviation, in the majority of the cases the difference is less than

Figure 8. GPC curve of the PS-4 sample (■) and the molecular mass distribution calculated by the GEX function (◆)

Figure 9. GPC curve of the PVC-4 sample (■) and the molecular mass distribution calculated by the GEX function (◆)

Figure 10. GPC curve of the PP-3 sample (■) and the molecular mass distribution calculated by the GEX function (◆)

10%. Based on these results we can conclude that using the model suggested by us it is possible (within the mentioned limits) it is possible to predict the molecular mass distribution from the rheological data. Individual constants are valid for each polymer, which cannot be predicted on generalized at the present state of knowledge.

6.4. Critical evaluation of the applicability of the model

Taking into account that the breadth of the molecular mass distribution functions of the polymers studied is moderate, it was investigated, whether a systematic variation of the Carreau parameters is reflected in the shape of the GEX distribution function and if yes, how. Therefore four cases were investigated, namely

- η_0 is varied, $\lambda = \text{constant}$, $M = \text{constant}$, and $N = \text{constant}$;
- λ is varied, $\eta_0 = \text{constant}$, $M = \text{constant}$ and $N = \text{constant}$;
- M is varied, $\eta_0 = \text{constant}$, $\lambda = \text{constant}$ and $N = \text{constant}$;
- N is varied, $\eta_0 = \text{constant}$, $\lambda = \text{constant}$ and $M = \text{constant}$.

Positive features of the model are as follows:

- (1) The increase/decrease of the maximum shear viscosity shifts the curve upwards/downwards along the molecular mass axis, the width of the distribution curve remains constant.

Table 8. A comparison of the constants of polymers calculated by the GEX model and those obtained from molecular mass distributions calculated from GPC test results

Polymer type	Calculated from the GEX model			Calculated from GPC tests			Relative difference* [%]		
	$\bar{M}_m$	$\bar{M}_n$	$\bar{M}_m/\bar{M}_n$	$\bar{M}_m$	$\bar{M}_n$	$\bar{M}_m/\bar{M}_n$	$\bar{M}_m$	$\bar{M}_n$	$\bar{M}_m/\bar{M}_n$
EDISTIR polystyrene									
PS-1	152776	60371	2.531	162634	64072	2.538	-6.06	-5.78	-0.29
PS-2	157475	52744	2.986	157532	58431	2.696	-0.04	-9.73	10.76
PS-3	171824	50492	3.404	160375	62151	2.580	7.14	-18.76	31.92
PS-4	191971	77761	2.469	176472	71525	2.467	8.78	8.72	0.07
PS-5	194411	61010	3.187	189487	88165	2.149	2.60	-30.80	48.29
PS-6	294751	108468	2.717	158968	58993	2.695	85.42	83.87	0.83
PS-7	156055	77134	2.023	131583	59117	2.226	18.60	30.48	-9.11
PS-8	177085	53343	3.320	150708	55342	2.723	17.50	-3.61	21.91
PS-9	216028	104523	2.067	187972	65438	2.873	14.93	59.73	-28.04
PS-10	150428	72491	2.075	150680	55797	2.701	-0.17	29.92	-23.16
PS-11	150765	88534	1.703	150798	53184	2.835	-0.02	66.47	-39.94
ONGROLIT PVC									
PVC-1	95600	48710	1.963	80035	40049	1.998	19.45	21.63	-1.77
PVC-2	92630	47868	1.935	106986	52384	2.042	-13.42	-8.62	-5.26
PVC-3	144287	55992	2.577	145541	68544	2.123	-0.86	-18.31	21.37
PVC-4	173043	78244	2.212	164508	80261	2.050	5.19	-2.51	7.92
PVC-5	191003	97504	1.959	188065	87418	2.151	1.56	11.54	-8.94
PVC-6	335544	148623	2.258	253923	114367	2.220	32.14	29.95	1.70
TIPPLEN polypropylene									
PP-1	125357	29412	4.262	121850	45274	4.701	2.88	-35.04	-9.34
PP-2	236460	53324	4.434	219166	46200	4.744	7.89	15.42	-6.53
PP-3	274656	63092	4.353	269912	55980	4.822	1.76	12.70	-9.72
PP-4	305930	58660	5.215	336073	68097	4.935	-8.97	-13.86	5.67
PP-5	526139	111638	4.713	480786	89048	5.399	9.43	25.37	-12.71
PP-6	762101	122382	6.227	617606	107993	5.719	23.40	13.32	8.88

*relative difference = $100 \cdot (\text{calculated from rheological tests} - \text{obtained from GPC tests}) / (\text{obtained from GPC tests})$

(2) An increase of the relaxation time results in broader distribution while a decrease leads to a narrower distribution.

(3) Increasing N intensifies the non-Newtonian character and results in a broader distribution, while its decrease causes a more Newtonian character and a narrower distribution function.

Negative characteristics of the model are that

(1) it can predict only narrow and moderately broad ($1.5 < \bar{M}_m/\bar{M}_n < 6$) distributions,

(2) the variation of M does not cause a significant change in the shape of the distribution function.

7. Conclusions

Determining the number- and mass distribution of commercial polystyrene, PVC and polypropylene samples by GPC method the constants of the distribution functions were calculated. From the shear viscosity function measured at 190°C by capillary viscometry the Carreau constants of the polymers were calculated. Equations for the maximum shear

viscosity and the mass average molecular mass taken from the literature were compared with our experimental data.

(1) The basic assumption of our model developed to a transform molecular mass distribution to shear viscosity function (direct problem) is that for each shear rate there is a M_c critical molecular mass. At $M < M_c$ the molecules contribute to the shear viscosity according to the $w_i M_i$ product, while at $M \geq M_c$ according to their mass fraction, as if their molecular mass were M_c . It is assumed further that the threshold value is independent of the average molecular mass of the sample and of the molecular mass distribution of the whole sample. Measured and calculated shear viscosity functions of the samples mentioned above agree within 10% error limit.

(2) In order to determine the molecular mass distribution function from the shear viscosity function measured by capillary viscometry (inverse problem) we used the shear viscosity function

of a two component polymer mixture developed by Bersted. Although the breadth of the distribution functions calculated by the modified Carreau equation approximates well the data derived from the GPC curves, the actual shape of the calculated distribution function and the deviation of measured and calculated mass and number average molecular masses is too high, therefore this model was not developed further.

- (3) In order to solve the inverse problem, i.e. for the prediction of the molecular mass distribution a model using the so-called GEX (General Exponential) function is suggested. The rheological model derived from the mathematical form of the distribution function assumed by Nobile is described by a 5-parameter GEX function. Having checked the validity of the model with a large number of polymer samples we concluded that it is possible to predict the molecular mass distribution from the rheological data with an accuracy of $\pm 30\%$. Individual constants are valid for every polymer, which cannot be generalized at our present state of knowledge.

The positive features of the model include that an increase/decrease of the maximum shear viscosity shifts the curve upwards/downwards the distribution function while the breadth of the distribution remains constant; the increase of the relaxation time leads to a broader, its increase to a narrower distribution; an increase of N increases the non-Newtonian character and broadens the distribution function, while its decrease decreases the non-Newtonian character and narrows down the distribution function. Negative features of the model include that it can predict only narrow to medium ($1.5 < \bar{M}_w/\bar{M}_n < 6$) distributions and a variation of M does not cause a significant change in the shape of the distribution function.

- (4) By solving the inverse problem a fast, but scientifically correct method is available for estimating the molecular mass distribution from macroscopic flow data without recourse to a lengthy dissolution process and a GPC test demanding expensive equipment and considerable experience.

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