A SIMPLE METHOD OF ESTIMATION OF THE POLYDISPERSITY INDEX OF NARROW MOLECULAR WEIGHT DISTRIBUTIONS BY USING QUASIELASTIC LIGHT SCATTERING DATA

Jaromír JAKEŠ

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences,
162 06 Prague 6

Received December 29, 1990
Accepted February 11, 1991

A simple method of estimation of the polydispersity index of narrow molecular weight distributions using quasielastic light scattering data has been suggested. The method approximates the relaxation times distribution by using the Pearson *V* distribution and iterates its parameters by the least squares method to an experimental correlation function. For the usual unimodal molecular weight distributions the polydispersity index estimate is good (with an error up to 0·1) at a determined value up to 1·2, rough at a determined value up to 1·5, while above this value the method is virtually impracticable. If the type of the molecular weight distribution is known (Schulz-Zimm, lognormal, Pearson *V*), the polydispersity value thus determined can be corrected, which would extend the applicability limits of the method. It is shown that for an adequate determination of the polydispersity index the noise level ought to be about 10^{-4}.

Determination of the polydispersity index M_w/M_n using quasielastic light scattering (QELS) data was dealt with by Han and McCrackin[1]. They assume either the Schulz-Zimm (SZ) or lognormal (LN) molecular weight distribution $W(M)$ and proportionality of the relaxation time, τ, to the square root of molecular weight, M; hence, by employing numerical integration, they calculate the autocorrelation function $g_1(t)$. After that, they try to find such parameters of molecular weight distribution (MWD) which would provide the best fit of the calculated function $g_1(t)$ with experiment. A disadvantage of such procedure is that it requires numerical integration over molecular weight distribution. A simpler method has been suggested by Štěpánek, Tuzar and Koňák[2]. They measured the relaxation function at several sampling times and, by using the least squares method, found for each sampling time an apparent relaxation time, assuming the sample to be monodisperse. They determined the polydispersity index by means of nomograms from the dependence of the apparent relaxation time on the sampling time by assuming that MWD is SZ or LN and that $\tau = cM^a$, a being 1/2, 1/3, or 0·577. A disadvantage of such procedure consists in that it requires measurement at several sampling times and nomographic reading off of the results. References to other papers devoted to the study of polydispersity by QELS can be found in the papers cited above[1,2].

In this study we report a very simple method of estimation of the polydispersity index of narrow MWD from QELS data which requires neither numerical integration nor nomographic reading off of the results, nor measurements at several sampling times. Due to its simplicity, the required calculation can be made very quickly using a calculator or a small computer.

THEORETICAL

In the case of narrow distributions the low resolution power of the QELS method (half a decade at best) does not allow us to determine the shape of the distribution (e.g., asymmetry), but only its width. Thus, the actual shape of the distribution is of little importance. For data treatment we choose the distribution Pearson *V* (P*V*), which allows the simplest mathematical procedure to be employed. The P*V* distribution is given by the relation

$$w(\tau) = \tau_0^p \tau^{-p-1} \exp(-\tau_0/\tau)/\Gamma(p) \tag{1}$$

with adjustable parameters τ_0, which determines the position of the distribution on the log τ axis, and p, which determines the width of the distribution. The Laplace transform of the P*V* distribution is given by

$$g_1(t) = \int_0^\infty w(\tau) \exp(-t/\tau)\, d\tau = (1 + t/\tau_0)^{-p}, \tag{2}$$

where t is the time delay. The extremely simple analytical form of the Laplace transform makes possible an easy iteration of the parameters τ_0 and p and of the position of the base line b from experimental data $g_1^2(t) + b$ obtained from the homodyne QELS experiment.

To determine the polydispersity index by using the parameter p mentioned above the usual assumptions are used, i.e., that macromolecules having molecular weight M scatter light whose intensity is proportional to the square of molecular weight and to their number, i.e. to $MW(M)$, where $W(M)$ is the weight molecular weight distribution with the relaxation time

$$\tau = cM^a, \tag{3}$$

where a, c are empirical parameters, a lying in the interval between 1/3 and 3/5. Hence, and also using the condition that the expressions $w(\tau)\, d\tau$ and $MW(M)\, dM$ must be proportional at $\tau = cM^a$, we obtain a relation between $w(\tau)$ and $W(M)$:

$$w(\tau) \sim W((\tau/c)^{1/a})\,(\tau/c)^{2/a-1}/(ac) \tag{4a}$$

$$w(cM^a)\, acM^{a-2} \sim W(M). \tag{4b}$$

For the P*V* distribution of relaxation times (*1*) we obtain for the polydispersity index

$$M_w/M_n = \Gamma(p)\,\Gamma(p + 2/a)/\Gamma^2(p + 1/a)\,. \qquad (5)$$

In particular, for the Gaussian statistical coil (polymer in the Θ solvent) with $a = 1/2$

$$M_w/M_n = (p + 3)\,(p + 2)/((p + 1)\,p) \qquad (5a)$$

and for rigid spheres with $a = 1/3$

$$M_w/M_n = (p + 5)\,(p + 4)\,(p + 3)/((p + 2)\,(p + 1)\,p)\,. \qquad (5b)$$

The method was used to estimate the polydispersity index of poly(methyl methacrylate) particles in ref.[3].

When using relation (*5*) to estimate the polydispersity index a question arises in which range of polydispersity and with what accuracy the relation can be employed, if the relaxation times distribution has a form different from P*V*. By using quite a long series of samples of macromolecules, it was shown in ref.[4] that the unimodal molecular weight distribution can be comparatively well approximated by a generalized exponential (GEX) distribution[5],

$$W(M) = |s|\, M^{u-1} M_0^{-u} \exp\left(-(M/M_0)^s\right)/\Gamma(u/s)\,, \qquad (6)$$

where parameters u and s are either both positive or both negative. In the limiting case $s \to 0$ the GEX distribution becomes[4] a LN distribution

$$W(M) = \pi^{-1/2} \beta^{-1} M^{-1} \exp\left(-\ln^2(M/M_0)/\beta^2\right) \qquad (7)$$

i.e. a distribution symmetrical in the $M \times W(M)$ vs $\log M$ plot. In the case of positive s the GEX distribution is asymmetrical with a wing at low M, in the case of negative s the wing is at high M. The parameter M_0 determines the position of distribution on the axis $\log M$ while the parameter u (β in the LN limit) determines the width of the distribution. The simultaneous change in the parameters u and s in the same ratio changes only the horizontal scale on the $\log M$ axis. For samples investigated in ref.[4] the parameter s was in the range between -1 and 1. For GEX MWD (Eq. (*6*)) we obtain from Eq. (*4a*) for the distribution function of relaxation times

$$w(\tau) \sim |s|\,(\tau/c)^{(u-1)/a}\, M_0^{-u} \exp\left(-((\tau/c)^{1/a}/M_0)^s\right)(\tau/c)^{2/a-1}/(ac) \qquad (8)$$

and after normalization

$$w(\tau) = |s'|\,\tau^{u'-1} \tau_0^{-u'} \exp\left(-(\tau/\tau_0)^{s'}\right)/\Gamma(u'/s')\,, \qquad (9)$$

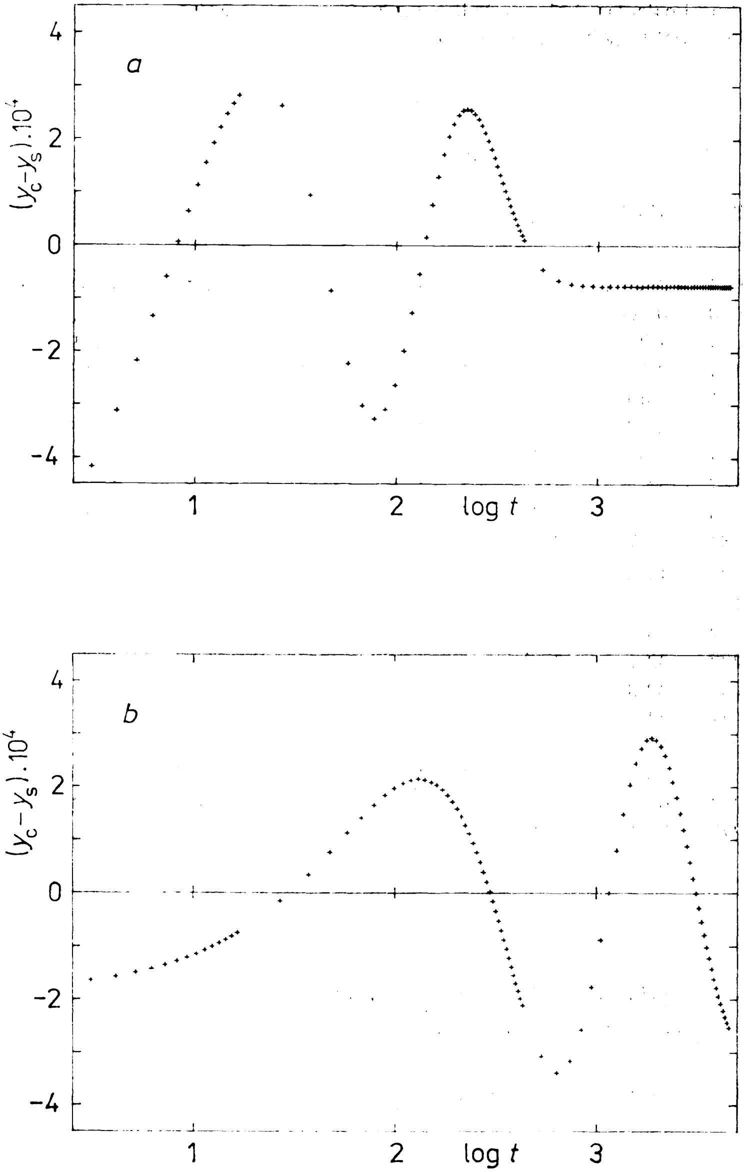

FIG. 1

Residuals of correlation functions (y_c calculated, y_s simulated) in the iteration of parameters of the Pearson *V* relaxation time distribution for *s'* 2, polydispersity index 2 (at $a = 1/2$), free iteration of the base and for *a* distribution $\tau \times w(\tau)$ maximum at $\tau = 100$, *b* distribution $\tau \times w(\tau)$ maximum at $\tau = 1\ 000$

TABLE I

Simulated (P_s) and calculated (P_c) polydispersity index values and the sum of squares of deviation for various GEX MWD and various a values

$a = 0·5$								
$s = 1·5$			$s = 1$ (SZ)			$s = 0·5$		
P_s	P_c	SSQ	P_s	P_c	SSQ	P_s	P_c	SSQ
1·042	1·039	0·0364	1·1	1·089	0·529	1·1	1·092	0·272
1·079	1·070	0·364	1·2	1·159	5·28	1·2	1·171	3·09
1·113	1·094	1·20	1·3	1·215	17·3	1·3	1·239	11·4
1·143	1·114	2·58	1·4	1·261	36·7	1·4	1·298	26·8
1·170	1·131	4·40	1·5	1·299	62·0	1·5	1·350	49·5
1·194	1·145	6·57	1·6	1·332	91·6	1·6	1·396	79·2
1·217	1·157	8·96	1·7	1·359	124	1·7	1·437	115
1·237	1·167	11·5	1·8	1·383	158	1·8	1·474	156
1·256	1·176	14·1	1·9	1·403	192	1·9	1·507	201
1·274	1·184	16·7	2·0	1·421	226	2·0	1·537	249
1·274[a]	1·191	17·8	2·0[a]	1·450	265	2·0[a]	1·569	256
1·274[b]	1·191	18·6	2·0[b]	1·449	276	2·0[b]	1·568	271
1·344	1·212	29·2	2·5	1·486	385	2·5	1·653	513
1·344[a]	1·222	32·1	2·5[a]	1·525	470	2·5[a]	1·702	551
1·394	1·230	39·8	3·0	1·527	515	3·0	1·734	782
1·394[a]	1·241	44·4	3·0[a]	1·572	646	3·0[a]	1·795	862
1·461	1·251	55·4	4·0	1·574	702	4·0	1·838	1 260
1·461[a]	1·264	63·2	4·0[a]	1·627	907	4·0[a]	1·918	1 440
1·504	1·263	66·0	5·0	1·600	827	5·0	1·903	1 640
1·504[a]	1·277	76·1	5·0[a]	1·659	1 090	5·0[a]	1·997	1 920

where $u' = (u + 1)/a$, $s' = s/a$, and $\tau_0 = cM_0^a$, i.e. again the GEX distribution. In the LN limiting case (Eq. (7)) we obtain

$$w(\tau) \sim \pi^{-1/2}\beta^{-1}(\tau/c)^{-1/a}\exp\left(-\ln^2\left((\tau/c)^{1/a}/M_0\right)/\beta^2\right)(\tau/c)^{2/a-1}/(ac) \qquad (10)$$

and

$$w(\tau) = \pi^{-1/2}\beta'^{-1}\tau^{-1}\exp\left(-\ln^2(\tau/\tau_0)/\beta'^2\right), \qquad (11)$$

where $\beta' = a\beta$ and $\tau_0 = cM_0^a\exp(a\beta^2/2)$, i.e. the LN distribution once again. Special cases of the GEX distribution are the SZ distribution ($s = 1$) and the PV distribution (Eq. (1), $s = -1$, $u = -p$).

TABLE 1

tions multiplied by 10^8 (SSQ) in the iteration of parameters of the P*V* relaxation time distribu-

$a = 0{\cdot}5$								
$s = 0$ (LN)			$s = -1$ (P*V*)			$s = -1{\cdot}5$		
P_s	P_c	SSQ	P_s	P_c	SSQ	P_s	P_c	SSQ
1·1	1·096	0·0785	1·1	1·104	0·104	1·045	1·046	0·0171
1·2	1·185	1·02	1·2	1·217	1·76	1·090	1·097	0·304
1·3	1·267	4·26	1·3	1·338	9·24	1·135	1·151	1·69
1·4	1·344	11·2	1·4	1·467	29·9	1·181	1·210	5·78
1·5	1·416	23·0	1·5	1·605	73·5	1·227	1·272	15·1
1·6	1·483	40·4	1·6	1·751	151	1·274	1·339	33·1
1·7	1·546	64·1	1·7	1·904	275	1·320	1·410	64·2
1·8	1·606	94·1	1·8	2·065	456	1·367	1·485	113
1·9	1·663	131	1·9	2·232	701	1·414	1·564	187
2·0	1·717	174	2·0	2·406	1 020	1·461	1·647	289
2·0[a]	1·747	138	2·0[a]	2·298	280	1·461[a]	1·604	108
2·0[b]	1·746	153	2·0[b]	2·310	512	1·461[b]	1·607	149
2·5	1·951	480	2·5	3·356	3 720	1·698	2·117	1 430
2·5[a]	2·006	377	2·5[a]	3·084	700	1·698[a]	1·998	364
3·0	2·142	911	3·0	4·400	7 920	1·937	2·664	3 930
3·0[a]	2·222	709	3·0[a]	3·906	1 140	1·937[a]	2·424	727
4·0	2·440	2 010	4·0	6·631	17 600	2·418	3·912	12 800
4·0[a]	2·571	1 560	4·0[a]	5·585	1 840	2·418[a]	3·326	1 480
5·0	2·668	3 290	5·0	8·941	25 000	2·902	5·272	24 500
5·0[a]	2·848	2 530	5·0[a]	7·253	2 240	2·902[a]	4·243	2 050

For the polydispersity index we obtain from Eqs (*8*) and (*9*) in ref.[4] (in which we substitute $u - 1$ for u for a different definition of this parameter)

$$M_w/M_n = \Gamma((u + 1)/s)\,\Gamma((u - 1)/s)/\Gamma^2(u/s) \qquad (12)$$

and in the LN limiting case from Eqs (*11*) and (*12*) in the same paper we have

$$M_w/M_n = \exp(\beta^2/2)\,. \qquad (13)$$

At last, by substituting $s = s'a$, $u = u'a - 1$, and $\beta = \beta'/a$ we obtain relations

TABLE I
(*Continued*)

$a = 1/3$								
$s = 1$ (SZ)			$s = 2/3$			$s = 1/3$		
P_s	P_c	SSQ	P_s	P_c	SSQ	P_s	P_c	SSQ
1·1	1·089	0·0364	1·253	1·206	0·529	1·246	1·214	0·272
1·2	1·161	0·364	1·577	1·377	5·28	1·538	1·408	3·09
1·3	1·219	1·20	2·001	1·520	17·3	1·886	1·582	11·4
1·4	1·267	2·58	2·577	1·640	36·7	2·300	1·738	26·8
1·5	1·308	4·40	3·395	1·741	62·0	2·793	1·879	49·5
1·6	1·343	6·57	4·638	1·828	91·6	3·382	2·006	79·2
1·7	1·372	8·96	6·729	1·904	124	4·088	2·121	115
1·8	1·398	11·5	10·942	1·969	158	4·937	2·226	156
1·9	1·421	14·1	23·644	2·027	192	5·965	2·322	201
2·0	1·441	16·7	∞	2·077	226	7·215	2·410	249
2·0^a	1·458	17·8	∞^a	2·159	265	7·215^a	2·505	256
2·0^b	1·458	18·6	∞^b	2·156	276	7·215^b	2·501	271
2·5	1·513	29·2	∞	2·263	385	20·000	2·759	513
2·5^a	1·538	32·1	∞^a	2·375	470	20·000^a	2·907	551
3·0	1·559	39·8	∞	2·380	515	82·964	3·007	782
3·0^a	1·588	44·4	∞^a	2·513	646	82·964^a	3·199	862
4·0	1·613	55·4	∞	2·519	702	∞	3·336	1 260
4·0^a	1·648	63·2	∞^a	2·680	907	∞^a	3·596	1 440
5·0	1·644	66·0	∞	2·599	827	∞	3·547	1 640
5·0^a	1·683	76·1	∞^a	2·776	1 090	∞^a	3·856	1 920

$$M_w/M_n = \Gamma((u' - 2/a)/s')\,\Gamma(u'/s')/\Gamma^2((u' - 1/a)/s')\,, \qquad (14)$$

$$M_w/M_n = \exp\left(\beta'^2/(2a^2)\right). \qquad (15)$$

By substituting $u' = -p$, $s' = -1$ we obtain equation (*5*).

RESULTS

To find out what error we would commit in the polydispersity index by approximating the distribution $w(\tau)$ with function (*1*), we simulated the correlation functions $g_1^2(t)$ for the GEX distributions $w(\tau)$ with the parameter $s' = -3, -2, 0, 1, 2, 3$ by means of the parameter u' chosen so as to make the polydispersity index 1·1, 1·2, ..., 2, 2·5,

TABLE I
(*Continued*)

$a = 1/3$								
$s = 0$ (LN)			$s = -2/3$			$s = -1$ (PV)		
P_s	P_c	SSQ	P_s	P_c	SSQ	P_s	P_c	SSQ
1·239	1·224	0·0785	1·228	1·243	0·104	1·1	1·106	0·0171
1·507	1·443	1·02	1·459	1·524	1·76	1·2	1·225	0·304
1·805	1·656	4·26	1·695	1·846	9·24	1·3	1·358	1·96
2·132	1·862	11·2	1·933	2·208	29·9	1·4	1·506	5·78
2·490	2·061	23·0	2·173	2·613	73·5	1·5	1·669	15·1
2·879	2·253	40·4	2·415	3·060	151	1·6	1·849	33·1
3·300	2·438	64·1	2·658	3·550	275	1·7	2·046	64·2
3·753	2·617	94·1	2·903	4·081	456	1·8	2·260	113
4·238	2·789	131	3·149	4·653	701	1·9	2·491	187
4·757	2·955	174	3·395	5·264	1 020	2·0	2·741	289
4·757^a	3·048	138	3·395^a	4·882	280	2·0^a	2·611	108
4·757^b	3·044	153	3·395^b	4·923	512	2·0^b	2·620	149
7·859	3·704	480	4·638	8·839	3 720	2·5	4·259	1 430
7·859^a	3·884	377	4·638^a	7·780	700	2·5^a	3·857	364
11·845	4·342	911	5·890	13·090	7 920	3·0	6·199	3 930
11·845^a	4·618	709	5·890^a	11·046	1 140	3·0^a	5·328	727
22·627	5·384	2 010	8·411	22·811	17 600	4·0	11·072	12 800
22·627^a	5·859	1 560	8·411^a	18·172	1 840	4·0^a	8·719	1 480
37·384	6·214	3 290	10·942	33·379	25 000	5·0	16·812	24 500
37·384^a	6·883	2 530	10·942^a	25·621	2 240	5·0^a	12·437	2 050

3,4,5 for $a = 1/2$ (for $a = 1/3$ in the case that $s = -3$ and 3) and by means of the parameter τ_0 chosen so as to make the maximum of the function $\tau w(\tau)$ lie at $\tau = 100$ (arbitrary time units, e.g., microseconds), and for the polydispersity index 2 and more also to have the maximum at $\tau = 1\,000$. The correlation functions were simulated at the points $t = 3, 4, 5, \ldots, 15, 16, 26, 36, \ldots, 406, 416, 516, 616, \ldots, 4\,316, 4\,416$ without noise. To these simulated correlation functions, parameters of the PV distribution with a freely iterated base were iterated (for a polydispersity index up to 2, also with a base subjected to the same experimental error as the other experimental points), and using the iterated parameter p the polydispersity index was calculated by means of Eq. (5).

The polydispersity index values thus obtained have been compared with those simulated in Table I together with the sum of squares of deviations in the iteration.

TABLE I
(Continued)

a = 0·6								
s = 1·8			s = 1·2			s = 0·6		
P_s	P_c	SSQ	P_s	P_c	SSQ	P_s	P_c	SSQ
1·029	1·027	0·0364	1·067	1·061	0·529	1·068	1·064	0·272
1·053	1·048	0·364	1·131	1·109	5·28	1·133	1·117	3·09
1·075	1·065	1·20	1·190	1·147	17·3	1·195	1·164	11·4
1·093	1·079	2·58	1·246	1·178	36·7	1·255	1·203	26·8
1·110	1·090	4·40	1·299	1·204	62·0	1·312	1·238	49·5
1·125	1·100	6·57	1·349	1·226	91·6	1·368	1·269	79·2
1·138	1·108	8·96	1·396	1·244	124	1·421	1·296	115
1·150	1·115	11·5	1·441	1·260	158	1·473	1·320	156
1·161	1·121	14·1	1·484	1·274	192	1·523	1·342	201
1·171	1·126	16·7	1·525	1·286	226	1·572	1·362	249
1·171[a]	1·131	17·8	1·525[a]	1·305	265	1·572[a]	1·383	256
1·171[b]	1·131	18·6	1·525[b]	1·304	276	1·572[b]	1·382	271
1·209	1·146	29·2	1·700	1·329	385	1·794	1·438	513
1·209[a]	1·152	32·1	1·700[a]	1·354	470	1·794[a]	1·469	551
1·235	1·158	39·8	1·841	1·355	515	1·988	1·490	782
1·235[a]	1·165	44·4	1·841[a]	1·385	646	1·988[a]	1·530	862
1·268	1·172	55·4	2·053	1·386	702	2·315	1·558	1 260
1·268[a]	1·180	63·2	2·053[a]	1·421	907	2·315[a]	1·610	1 440
1·289	1·180	66·0	2·204	1·403	827	2·583	1·600	1 640
1·289[a]	1·189	76·1	2·204[a]	1·442	1 090	2·583[a]	1·660	1 920

[a] Maximum of the $\tau \times w(\tau)$ distribution simulated at 1 000 instead of the standard value 100.
[b] As the note [a] and further with the base iterated with the same experimental error as the other

The results of iteration with the experimental base differed only very little from those obtained with the freely iterated base, and are therefore given only for the polydispersity index 2 and the maximum of the function $\tau w(\tau)$ at $\tau = 1\,000$. The course of the residuals in the iteration at a fixed maximum of the function $\tau w(\tau)$ and at a polydispersity index up to 2 is very similar, the main difference being the scale and the sign according to the sign at $s' + 1$. This course can be seen in Fig. 1 for $s' = 2$, polydispersity index 2 (at $a = 1/2$) and free iteration of the base.

DISCUSSION

Values in Table I show that the method underestimates the polydispersity index

TABLE I
(*Continued*)

$a = 0·6$								
$s = 0$ (LN)			$s = -1·2$			$s = -1·8$		
P_s	P_c	SSQ	P_s	P_c	SSQ	P_s	P_c	SSQ
1·068	1·066	0·0785	1·070	1·072	0·104	1·031	1·032	0·0171
1·135	1·127	1·02	1·139	1·149	1·76	1·063	1·067	0·304
1·200	1·182	4·26	1·209	1·230	9·24	1·095	1·104	1·69
1·263	1·234	11·2	1·279	1·316	29·9	1·128	1·144	5·78
1·325	1·282	23·0	1·349	1·407	73·5	1·161	1·186	15·1
1·386	1·326	40·4	1·419	1·501	151	1·194	1·231	33·1
1·446	1·368	64·1	1·489	1·600	275	1·228	1·278	64·2
1·504	1·407	94·1	1·560	1·703	456	1·262	1·328	113
1·562	1·444	131	1·630	1·809	701	1·296	1·380	187
1·618	1·479	174	1·700	1·919	1 020	1·330	1·434	289
1·618[a]	1·499	138	1·700[a]	1·851	280	1·330[a]	1·406	108
1·618[b]	1·498	153	1·700[b]	1·858	512	1·330[b]	1·408	149
1·890	1·631	480	2·053	2·507	3 720	1·505	1·737	1 430
1·890[a]	1·665	377	2·053[a]	2·340	700	1·505[a]	1·660	364
2·145	1·752	911	2·406	3·138	7 920	1·683	2·080	3 930
2·145[a]	1·803	709	2·406[a]	2·841	1 140	1·683[a]	1·930	727
2·619	1·940	2 010	3·113	4·463	17 600	2·043	2·845	12 800
2·619[a]	2·022	1 560	3·113[a]	3·845	1 840	2·043[a]	2·488	1 480
3·058	2·083	3 290	3·820	5·813	25 000	2·406	3·660	24 500
3·058[a]	2·194	2 530	3·820[a]	4·828	2 240	2·406[a]	3·045	2 050

experimental points instead of the standard free iteration of the base.

values for $s > -a$ (i.e. for SZ and LN MWD) while overestimating those for $s < -a$ (P*V* MWD). For a polydispersity index up to 1·2 the method gives a good estimate with an error below 0·1; at a fixed s value the error is only little dependent on a. For the polydispersity indices above this value up to 1·5 the method still gives a very rough estimate of the polydispersity index (e.g. the real polydispersity index 2 in the case of SZ MWD is distorted to c. 1·45), while above this value the method is virtually not applicable at all without some additional steps. If, however, we know the MWD type (SZ, LN, P*V*, or s in the case of GEX), or if we assume some MWD type, then by using Table I we can correct the calculated polydispersity index values, thus extending applicability of the method.

If the sum of the squares of the residuals (shown multiplied by 10^8 as SSQ in Table I) is lower than the square of the noise level (i. e. than the average square of the experimental error) in the correlation function $g_1^2(t)$, then by using this correlation function it is not possible to distinguish the simulated (real) distribution from the assumed one. At the usual noise level about 10^{-3} this means that at the polydispersity index up to c. 2 QELS cannot be used to determine the MWD type. The worst situation arises at $a = 1/3$, because in this case the relaxation times distribution at the same MWD is narrowest. From SSQ values in Table I we can see that in order to determine the polydispersity index from the QELS experiment with sensible accuracy, we would have to reach a noise level in the correlation function of about 10^{-4}, which can be achieved only by a very long measurement using the best correlators.

REFERENCES

1. Han C. C., McCrackin F. L.: Polymer *20*, 427 (1979).
2. Štěpánek P., Tuzar Z., Koňák Č.: Collect. Czech. Chem. Commun. *52*, 1235 (1987).
3. Stejskal J., Kratochvíl P., Koubík P., Tuzar Z., Urban J., Helmstedt M., Jenkins A. D.: Polymer *31*, 1816 (1990).
4. Jakeš J., Saudek V.: Makromol. Chem. *187*, 2223 (1986).
5. Kubín M.: Collect. Czech. Chem. Commun. *32*, 1505 (1967).

Translated by L. Kopecká.