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Pulsed Initiation Polymerization as a Means of Obtaining Propagation Rate Coefficients in Free-Radical Polymerizations

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Pulsed Initiation Polymerization as a Means of Obtaining Propagation Rate Coefficients in Free-Radical Polymerizations

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1. INTRODUCTION

The knowledge of kinetic coefficients in polymerization is of paramount importance for the modern production of polymers. Not only the rate of reaction of a polymerization is determined by the kinetics, but also the molecular weight (M_w) distribution and, in copolymerization, the chemical composition distribution.

One of the most primary and important coefficients is the propagation rate coefficient k_p . In most kinetic analysis, a combination of k_p and the termination rate coefficient k_t is determined. Knowledge of k_p makes separation of both coefficients possible. The rate of chain propagation is determined by k_p , therefore there is always a direct link between molecular weight and k_p . In general, Eq. 1 describes the molecular weight as a function of k_p .

$$M_w = k_p [M] M_0 t_g \quad (1)$$

where $[M]$ represents the monomer concentration at the site of polymerization, M_0 the molecular weight of the monomeric unit, and t_g the time of growth of a polymer chain.

The time of growth of a polymer chain is determined by chain growth stopping events like bimolecular termination or transfer of radical chain end activity (e.g., to monomer or other species). In the last decade, this simple equation has also been applied to obtain values for k_p . From Eq. 1, when the molecular weight of the formed polymer can be measured and the time of growth of a polymer chain is known, k_p can easily be determined.

One means of knowing and controlling the time of growth of a polymer chain is by pulsed initiation and termination. One can, for example, use pulses of electrons or γ radiation, which generate many radicals in a short time span and render initiation and termination. The time between these pulses will be the time of growth for at least a part of the formed polymer chains. Another method to generate radicals on a short time scale is the use of photoinitiators, which are decomposed by short pulses of laser light in a method that is called pulsed laser polymerization (PLP). In combination with molecular weight analysis by means of size-exclusion chromatography (SEC), this is a powerful method of obtaining values for k_p . Other methods comprising pulsed initiation are the single-pulse time-resolved pulsed-laser polymerization (TR-PLP), the rotating sector method, and spatially intermitted polymerization (SIP); these methods are briefly discussed also.

2. THE PULSED LASER POLYMERIZATION/SIZE-EXCLUSION CHROMATOGRAPHY METHOD

2.1. Description of the Method

Determination of the propagation rate coefficients is preferably performed by the PLP technique combined with SEC. This method is very suitable for obtaining accurate propagation rate coefficients in homogeneous systems because there are very few assumptions made and the determination yields a value of k_p not coupled to the termination coefficient k_t , in contrast to other techniques. For this reason, extensive reference is made to the literature on this relatively new method. The PLP/SEC technique was described originally by Genkin and Sokolov [1] and Alexandrov et al. [2] in 1977 and was further developed by Olaj and coworkers in 1987 and the years after [3–9]. This method comprises the generation of radicals through a photoinitiator, activated by a laser pulse. The time of growth of a polymer chain is directly determined by the time between pulses; this experiment gives direct access to k_p . The method is schematically illustrated in Fig. 1.

The degree of propagation for the chains initiated and terminated by short pulses of radicals induced by light (in combination with a photoinitia-

FIG. 1. Schematic representation of the pulsed laser polymerization experiment.

tor) or radical-generating radiation like electron beams or γ radiation is given by the simple equation [3]

$$L_{0,i} = i^* k_p^* [M]^* t_p \quad (2)$$

where $L_{0,i}$ is the chain length of the polymer formed in the process of growth in the time between two radical pulses and t_p is the time between two subsequent radical pulses, which is assumed to be equal to t_g (Eq. 1) and $i = 1, 2, 3, \dots$. The higher order peaks ($i = 2, 3, \dots$) may occur when growing chains survive termination by one or more subsequent pulses. The radical profile as a function of time in a pulsed laser experiment is schematically shown in Fig. 2.

Between two pulses, normal bimolecular termination can occur, which results in the so-called background polymer. Olaj, Bitai, and Hinkelmann [3] suggested that the inflection point at the low molecular weight side of the peaks gives a good measure for k_p . This is usually true; however, in very small microemulsion droplets, indications were found that the best measure for k_p shifts from the inflection point to the peak maximum (see below). On the other hand, when the k_p is known, Eq. 2 can also be used to obtain the monomer concentration in microemulsion droplets and in latex particles. In Fig. 3, a typical molecular weight distribution is shown for polymer produced in a PLP experiment.

FIG. 2. Radical concentration profile (schematically) in a pulsed laser polymerization experiment (— homogeneous medium, ···· microemulsions or latex systems).

FIG. 3. Molecular weight distribution of polystyrene obtained in a pulsed laser polymerization (PLP) experiment at 40°C and at a frequency of 10 Hz in bulk. (After Ref. 52.)

2.2. Overview of Publications to 1997

An overview of the publications to the beginning of 1997 of the other active groups in PLP/SEC is given next.

Davis, O'Driscoll, and coworkers [10–19] extended the method to copolymerization; the average propagation rate coefficient $\langle k_p \rangle$ is given by the general equation

$$\langle k_p \rangle = \frac{\bar{r}_1 f_1^2 + 2f_1 f_2 + \bar{r}_2 f_2^2}{(\bar{r}_1 f_1 / \bar{k}_{11}) + (\bar{r}_2 f_2 / \bar{k}_{22})} \quad (3)$$

where, in the ultimate model, $\bar{r}_1 = r_1, \bar{r}_2 = r_2, \bar{k}_{11} = k_{11}, \bar{k}_{22} = k_{22}$, with

$$r_1 = \frac{k_{11}}{k_{12}} \quad \text{and} \quad r_2 = \frac{k_{22}}{k_{21}}$$

In the case that the penultimate unit also influences the reactivity, the penultimate model applies, and we can also define k_{111} , k_{211} , and so on in Eq. 3:

$$\bar{k}_{11} = \frac{k_{111}(f_1 r_1 + f_2)}{f_1 r_1 + f_2 / s_1} \quad \text{and} \quad \bar{k}_{22} = \frac{k_{222}(f_2 r_2 + f_1)}{f_2 r_2 + f_1 / s_2}$$

$$\bar{r}_1 = \frac{r'_1(f_1 r_1 + f_2)}{f_1 r'_1 + f_2} \quad \text{and} \quad \bar{r}_2 = \frac{r'_2(f_2 r_2 + f_1)}{f_2 r'_2 + f_1}$$

$$r_1 = \frac{k_{111}}{k_{112}}, r_2 = \frac{k_{222}}{k_{221}}, r'_1 = \frac{k_{211}}{k_{212}}, r'_2 = \frac{k_{122}}{k_{121}}, s_1 = \frac{k_{211}}{k_{111}}, s_2 = \frac{k_{122}}{k_{222}}$$

O'Driscoll and Kuindersma simulated the PLP experiments with Monte Carlo simulations [15], and Zammit, Davis, and Haddleton investigated the molecular weight of the resulting polymer from a PLP experiment of methyl methacrylate (MMA) with matrix-assisted laser desorption [17]. Buback's group [20–26] also performed PLP experiments at high pressures with subsequent SEC analysis. In 1986, a working party of the International Union of Pure and Applied Chemistry (IUPAC), Modeling of Free Radical Polymerization Kinetics and Processes, was founded that recommended the PLP/SEC method as the most reliable method for the determination of k_p [27–31]. At low radical concentrations, the transfer rate coefficient to monomer or transfer agent can be inferred from the molecular weight distribution. It is found that transfer to monomer is a dominant process in, for example, methyl acrylate (MA) polymerization. Gilbert and coworkers [32–39] determined the transfer rate coefficients in conjunction with the PLP experiment [37, 38].

Another active group is that of Hutchinson [40–46]. They simulated the PLP experiment to support their experimental efforts, especially problems with transfer and rapid termination [41, 43]. Holdcroft and Guillet were the first to perform PLP in transparent microemulsions [47]. This was also done by the group of van Herk and German [48–53] in collaboration with the group of Schweer. Van Herk and coworkers performed pulsed electron beam polymerization in heterogeneous systems [53], following the same principles as in the PLP/SEC method.

The group of Schweer [54–60] published simulations of the PLP experiment and also used a flashlight instead of a pulsed laser to do similar experiments [54]. They collaborated with the group of van Herk and German on the issue of PLP in heterogeneous systems like microemulsions and latex particles [48, 49, 56]. Recently, they also applied the matrix-assisted laser desorption ionization–time of flight technique (MALDI-TOF) technique to determine the molecular weight distribution [60].

The group of Moad [61, 62], besides PLP/SEC experiments, also published some simulations [62]. Other groups active in the field of simulations of PLP experiments are Yan, Zhang, and Schweer [63], Zhang, Yang, and coworkers [64, 65], and the group of McLaughlin and Hoyle [66]. The last group published several papers on the complete molecular weight distributions formed during a PLP experiment, but not with the direct aim of determining k_p values [66, 67].

Two general reviews on laser-initiated polymerization, including pulsed laser polymerization, to obtain values for k_p were published by Davis and coworkers [18, 19].

Although the PLP/SEC method can result in accurate k_p values, there are some problems. The method relies on accurate SEC calibration. If narrow molecular weight standards are not available, the method of universal calibration can be applied, which again relies on the knowledge of the Mark-Houwink constants [44, 45]. One solution to this problem is the use of an in-line viscosity detector. The values for the Mark-Houwink constants are regularly updated, which therefore also updates the values of k_p (see, e.g., Ref. 44).

Another problem occurs with fast-reacting monomers like vinylacetate or methyl acrylate and butyl acrylate (BA) [45, 68]. The occurrence of clear peaks in the SEC trace that can be attributed to chains that are initiated and terminated by laser-generated radicals can be hindered by the following processes: (1) preliminary termination of the growing chains by rapid termination or chain transfer to a monomer or polymer, and (2) little termination by the small laser-generated radicals because of a slow termination rate or because of insufficient penetration of the laser beam in the sample.

An example of the first situation might be occurring in the case of vinylacetate and butyl acrylate [45]. The second situation can occur in systems in which there is a strong light adsorption, for example, in heterogeneous systems like dispersions of latex particles [49]. There it was observed that stirring the sample rendered the SEC trace featureless because the radicals generated in the region where the light could still penetrate are transported to the dark region where only "normal" termination can occur [49]. A solution for these systems can be the use of alternative sources of radicals like γ radiation or electron beams [53].

2.3. Homopropagation Rate Coefficients

In Table 1, a compilation of the latest (to the end of 1996) k_p values and activation parameters is given that were obtained with the PLP/SEC method. The reliability of the entries in Table 1 depends on the calibration procedure used for the SEC and on the number of data points and the temperature range. For more information, the reader should refer to the original publications. Those entries that are the most reliable, according to the author's judgment, are labeled with a star. The IUPAC-recommended values, which are a composed of a combined fit of data from different laboratories, are labeled with two stars.

In most cases, the low molecular weight inflection point is the best measure of k_p , as is also confirmed by several simulations [15, 63]. From the modeling studies of Sarnecki and Schweer [57] and Manders, van Herk,

TABLE 1

Homopropagation Rate Coefficients Obtained by the PLP/SEC Method
(A in $\text{L}^{-1} \text{mol}^{-1} \text{s}^{-1}$, Ea in kJ mol^{-1} , k_p in $\text{L}^{-1} \text{mol}^{-1} \text{s}^{-1}$)

Monomer	Solvent	Arrhenius A	eq. Ea	10 °C	25 °C	30 °C	40 °C	50 °C	60 °C	70 °C	ref
Acrylamide	water, pH=1		20		16000						32
Methacrylam.	Water, pH=1		20		1100						32
BA	bulk	$2.51 \cdot 10^7$	20								37
BA	THF/toluene	$1.66 \cdot 10^7$	17.27	10800	15600	17500	21800	26800	32500	39000	39
BA*	bulk	$1.8 \cdot 10^7$	17.4	11100	16100	18100	22500	27700	33700	40400	68
n-BMA	bulk, 1000 bar	$7.28 \cdot 10^6$	22.9	434	708	824	1100	1450	1870	2380	22
n-BMA	bulk	$3.44 \cdot 10^6$	23.3		274						13
n-BMA	bulk	$1.81 \cdot 10^6$	20.55	289	454	523	676	857	1108	1394	42
n-BMA*	bulk	$2.47 \cdot 10^6$	21.8	235	374	433	570	739	943	1190	44
t-BMA	bulk	$2.51 \cdot 10^7$	27.7		352			836			36
i-BMA	bulk	$2.47 \cdot 10^6$	21.53	252	417	496	633	798	1040	1336	42
i-BMA*	bulk	$2.96 \cdot 10^6$	22.46	213	344	399	531	693	891	1130	44
Butadiene	chlorobenzene	$8.05 \cdot 10^7$	35.71	20.8	44.6	56	85	138	204	295	54
Chloroprene	bulk	$1.95 \cdot 10^7$	26.63	235	447	485	673	988	1300	1720	40
DA	bulk			17660		22113					45
DA	bulk, 100 bar	$1.09 \cdot 10^7$	15.8	13300	18600	20700	25300	30500	36400	43000	68
DMA	toluene	$2.93 \cdot 10^5$	16.19	300	427	452	601	796	848	1010	13
DMA*	bulk	$3.44 \cdot 10^6$	21.72	339	538	622	819	1060	1350	1700	44
EHA	bulk			13180	18030						45
EMA	bulk	$1.50 \cdot 10^6$	20.46		258						13
EMA*	bulk	$3.2 \cdot 10^6$	22.8	206	324	400	590	676	939	1160	44
PMOS	toluene	$5.90 \cdot 10^5$	23.0	33.7	52	64.2	85.9	113	146	186	12
MA	bulk, 100 bar	$3.61 \cdot 10^5$	13.9	9860	13300	14600	17400	20500	24000	27700	68
MAA*	methanol	$6 \cdot 10^5$	17.7	326	477	536	671	828	1009	1215	46
MAN	bulk/benzene	$2.69 \cdot 10^6$	29.7	8.9	16.8	20.5	29.9	42.5	59.3	81	61
MMA	bulk	$2.39 \cdot 10^6$	22.18	193	311	360	470	621	769	989	40
MMA	bulk	$4.94 \cdot 10^6$	23.94		316			667			23
MMA	toluene					384					21
MMA	bulk				294						10
MMA	bulk					364					20
MMA	bulk				313						5
MMA*	bulk	$1.85 \cdot 10^6$	21.31	217	342	394	516	664	843	1050	44
MMA**	bulk	$2.65 \cdot 10^6$	22.34	200	323	375	497	649	833	1050	31
¹ H ₈ -MMA	bulk				270						7
² H ₈ -MMA	bulk				342						7
Sty	bulk				77						5
Sty	toluene				79						5
Stv	bulk				78						10
Sty	bulk	$1.99 \cdot 10^7$	30.78	41.7	80.6	98.9	146	211	297	411	13
Stv	bulk					107		260		479	40
Stv	bulk	$3.04 \cdot 10^7$	31.48			116		248		490	26
Sty*	bulk	$4.57 \cdot 10^7$	32.6	44.2	88.8	110	167	246	353	498	52
Sty**	bulk	$4.27 \cdot 10^7$	32.51	42.9	85.9	107	161	237	341	480	30
Vinylacetate	bulk	$2.7 \cdot 10^8$	27.82	1935	3420						42
Vinylacetate*	bulk	$1.49 \cdot 10^7$	20.39	2580	3990	4570	5910	7540	9460	11700	44

* Most reliable values, based on the use of the most recent Mark-Houwink constants and/or the highest accuracy of the experiments

** IUPAC values, usually a combined fit of data from several laboratories

Italics, values calculated from the Arrhenius parameters

and German [51], it turns out that under certain experimental conditions the maximum of the PLP peaks can be the best measure of k_p , especially when high radical concentrations are present in the system under investigation, for example, in the very small microemulsion droplets [48]. In microemulsion droplets and latex particles, the radical concentration profile (Fig. 2) in the pseudostationary state will consist of two decay curves following the rapid increase in radical concentration after the laser pulse. In the first curve, just after the rapid increase in the radical concentration, the rate of termination will be higher in the (micro)emulsion droplets or particles because the local radical concentration will be higher. The second decay curve comprises the stage at which the number of radicals per particle is less than two; here, the termination rate will be lower than in a homogeneous system because termination involves exit of a radical and entry into another particle, followed by bimolecular termination.

Besides laser initiation/termination, some alternative sources of initiation and termination were investigated with the same purpose of obtaining k_p values; Olaj and Schnöll-Bitai investigated the periodic variation of initiation by dropwise addition of initiator [69] and the periodic variation of termination by addition of a radical scavenger [70]. Olaj, Kremminger, and Schnöll-Bitai [71, 72] also analyzed the molecular weight distribution of polymer obtained in a rotating sector experiment, which compared well with that from PLP. Van Herk et al. applied an electron beam as a source for radicals in a study on latex particles [53], and Schweer and coworkers applied a flashlight to generate radicals through a photoinitiator [54, 55]. Holdcroft and Guillet [73] controlled the initiation and termination processes independently in a dual-laser technique in which two laser pulses of different wavelengths were used with the aim of producing monodisperse polymer.

2.4. Copolymerization Rate Coefficients

There are several copolymerization systems investigated with the PLP/SEC method [7, 11–13, 72, 74]. Even more so than in the case of homopolymerization, calibration of the SEC equipment introduces problems. A compilation of the systems investigated and the observed reactivity ratios is given in Table 2.

A major problem arises with the Mark–Houwink coefficients used by Davis, O'Driscoll, and coworkers [13] for the acrylates (MA and BA). Beuermann et al. [45] showed that the literature values used by Davis, O'Driscoll, and coworkers need to be adjusted rather dramatically. Because of the general problems with the PLP method applied to acrylates [45], combined with the new values for the Mark–Houwink constants, the homo-

TABLE 2

Copolymerization Parameters Obtained by the PLP/SEC Method (k_p in $L^{-1} mol^{-1} s^{-1}$)

Monomer 1	Monomer 2	Solvent	T (°C)	$k_{(1)11}$	$k_{(2)22}$	r_1	r_2	r_1'	r_2'	s_1	s_2	ref
1H_8 -MMA	2H_8 -MMA	bulk	25	270	342	1	1	-	-	-	-	7
Sty	MMA	bulk	25	89.1	299.2	0.523	0.460	0.523	0.460	0.30	0.80	72
Sty	MMA	bulk	25	77.5	294	0.472	0.454	0.472	0.454	0.466	0.175	11
Sty	EMA	bulk	25	78	258	0.62	0.35	0.62	0.35	0.62	0.21	13
Sty	EMA	bulk	55	249	589	0.62	0.35	0.62	0.35	0.45	0.22	13
Sty	BMA	bulk	25	78	274	0.72	0.45	0.72	0.45	0.56	0.63	13
Sty	BMA	bulk	55	249	656	0.72	0.45	0.72	0.45	0.50	0.67	13
Sty	DMA	toluene	25	78	776	0.57	0.45	0.57	0.45	0.33	0.26	13
Sty	MA	bulk	25	78	-	0.73	0.19	0.73	0.19	1.10	0.26	13
Sty	MA	bulk	50	-	-	0.73	0.19	0.73	0.19	0.94	0.11	13
Sty	BA	bulk	25	78	-	0.95	0.18	0.95	0.18	1.89	0.21	13
Sty	BA	bulk	50	-	-	0.95	0.18	0.95	0.18	0.90	0.11	13
MMA	BA	bulk	60	847	33880	2.15	0.40	2.15	0.40	1.98	0.43	74
PMOS	Sty	toluene	25	52	86	0.82	1.12	-	-	-	-	12
PMOS	MMA	toluene	25	52	300	0.32	0.29	0.32	0.29	0.36	0.60	12

propagation rate coefficients used by Davis, O'Driscoll, et al. might differ by a factor of 5–7 from the actual ones. Therefore, the entries in Table 2 regarding the acrylates in Ref. 13 are not reliable.

A special system in which one of the monomers does not homopolymerize is the system styrene (Sty)/maleic anhydride, in which maleic anhydride does not homopolymerize [16]. The first terpolymerization system that was investigated with the PLP/SEC method is the system styrene/methyl methacrylate/methyl acrylate [50]. Recently [75], pronounced solvent effects were observed for the system Sty/MMA in benzyl alcohol using the PLP/SEC technique in combination with composition data and sequence distributions. Olaj et al. showed that the molecular weight distribution obtained in a rotating sector experiment can be used just as well to obtain k_p values from the molecular weight distribution [71, 72].

3. THE TIME-RESOLVED PULSED-LASER POLYMERIZATION METHOD

In 1986 [76], with the advent of powerful ultraviolet (UV) lasers, a new method was introduced that is capable of determining k_p and the termination rate coefficient (k_t): time-resolved pulsed-laser polymerization (TR-PLP). In this method, the conversion of the monomer is followed as a function of time t , for example, with an infrared detector after the genera-

tion of radicals with a short laser pulse. The monomer concentration $[M]_t$ as a function of time is given by

$$[M]_t/[M]_0 = (2k_t[R]_0 t + 1)^{-0.5k_p/k_t} \quad (4)$$

with $[R]_0$ the radical concentration immediately after laser pulse absorption, which can be calculated from the absorbed laser energy if the quantum yield is known. With known $[R]_0$, the value for k_t , and thus for k_p , can be inferred. A combination of the obtained ratio k_p/k_t with independently determined k_p data (e.g., obtained with the PLP/SEC method) gives k_t values.

Another method using pulsed laser initiation is that in which the overall polymerization rate is measured for a pulsed laser polymerization with a pulse frequency ν [77, 78]. A pseudostationary-state radical concentration $[R]_{max}$ can be substituted in Eq. 4 and time $t = 1/\nu$. By variation of the pulse frequency ν , again k_p/k_t and $k_t[R]_{max}$ can be obtained. The quantum yield can be obtained when it is possible to determine quantitatively the end groups introduced by the photoinitiator [79, 80].

4. THE ROTATING SECTOR METHOD AND SPATIALLY INTERMITTENT POLYMERIZATION

Analysis of the steady-state kinetic expression does allow the determination of the ratio k_p^2/k_t . The rate of polymerization (R_p) is given by

$$R_p = -\frac{d[M]}{dt} = k_p[R][M] = k_p\left(\frac{fk_d[I]}{k_t}\right)^{1/2} [M] \quad (5)$$

where f is the initiator efficiency and k_d the rate of initiator decomposition.

The average lifetime τ of the growing chain during (pseudo)stationary-state conditions is given by

$$\tau = \frac{[R]_s}{2k_t[R]_s^2} = \frac{1}{2k_t[R]_s} = \frac{k_p[M]}{2k_t R_p} \quad (6)$$

A measurement of τ in conjunction with R_p will yield the ratio k_p/k_t . The oldest and most widely used method is that of the rotating sector. In this method, first applied by Burnett and Melville [81], the irradiation of a photoinitiated radical polymerization is modulated by a rotating sector, with illumination and dark periods produced by portions cut out of the disk. In a typical experiment, the average rate of polymerization is measured as a function of the speed of the rotating sector, expressed in Δt , the

period of irradiation. The plot of R_p as a function of $\Delta t/\tau$ can be compared with theoretical curves, and resulting value of τ , in combination with steady-state experiments, can then be used to evaluate k_p and k_t . An important drawback of this method is that, because termination is diffusion controlled, k_t is a function of chain length and viscosity, and it is difficult, if not impossible, to have identical reaction conditions in both experiments. For a long time in copolymerization, the variations in the ratio k_p/k_t were ascribed (erroneously) to the termination rate coefficients, but as the termination process is not chemically controlled, this is very unlikely. Ma, Fukuda, and Inagaki [82] introduced the penultimate model for the propagation step (Eq. 4). Another form of this experiment is spatially intermittent polymerization (SIP) [83].

5. CONCLUSIONS

The quality of modern polymer production benefits from accurate modeling of polymerization processes, for which the accurate knowledge of kinetic parameters is essential. The pulsed initiation polymerization method is a relatively new and valuable method to obtain propagation rate coefficients; the number of publications dealing with this method is rapidly increasing, leading to more and more accurate kinetic constants. Prediction and control of the microstructure of the formed (co)polymer has improved due to the improvement of the methods of obtaining kinetic and thermodynamic parameters relevant to homogeneous and heterogeneous polymerization. This development will also have its impact on the possibilities of designing intelligent process strategies aimed at obtaining well-defined products with better properties [84].

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MONOMER ABBREVIATIONS

BA	butyl acrylate
<i>n</i> -BMA	<i>n</i> -butyl methacrylate
<i>t</i> -BMA	<i>t</i> -butyl methacrylate
<i>i</i> -BMA	<i>i</i> -butyl methacrylate
DA	dodecyl acrylate

DMA	dodecyl methacrylate
EHA	2-ethylhexyl acrylate
EMA	ethyl methacrylate
PMOS	<i>p</i> -methoxystyrene
MA	methyl acrylate
MAA	methacrylic acid
MAN	methacrylonitrile
MMA	methyl methacrylate
Sty	styrene

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