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Solvent Effects on the Rate Constant of Chain Propagation in Free Radical Polymerization

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Summary. Using pseudostationary techniques (pulsed laser polymerization followed by an analysis of the chain-length distribution), the rate constant of chain propagation k_p was directly determined for 1:1 mixtures of the monomer and a number of solvents for styrene and methyl methacrylate as well as for a 1:1 comonomer system of these two monomers, thus reducing the bulk monomer concentration to half of its bulk value in all cases. The presence of solvent emerged to be of moderate influence on k_p only, the effects never exceeding 20% in either direction. Depressions of k_p were more frequent than elevations. The results did not favour one of the existing theories (EDA-complex theory, hot radical theory) over the other. In case of a bad solvent, k_p may rather reflect changes in the local monomer concentration at the site of reaction caused by preferential solvation by the monomer which constitutes the better "solvent".

Keywords. Methyl methacrylate; Pulsed laser polymerization; Radical solution polymerization; Rate constant of propagation; Solvent effects; Styrene.

Lösungsmitteleinfluß auf die Geschwindigkeitskonstante des Kettenwachstums in der radikalischen Polymerisation

Zusammenfassung. Mit Hilfe einer pseudostationären Technik (Anregung durch periodische Laserpulse und anschließende Analyse der Kettenlängenverteilung) wurde die Geschwindigkeitskonstante des Kettenwachstums k_p für 1:1-Gemische des Monomeren mit einer Reihe von Lösungsmitteln bestimmt; als Monomere wurden Styrol und Methylmethacrylat sowie eine 1:1-Mischung dieser beiden (als Comonomere) eingesetzt, sodaß die Monomerkonzentration in allen Fällen die Hälfte der Monomerkonzentration in Substanz betrug. Die Größe von k_p wurde durch die Anwesenheit eines Lösungsmittels nur mäßig beeinflußt: die Effekte überschritten in keinem Fall 20%, weder in der einen noch in der anderen Richtung. Herabsetzungen von k_p treten dabei häufiger auf als Erhöhungen. Die Resultate der Lösungspolymerisation begünstigen keine der existierenden Theorien (EDA-Komplex-Theorie, *hot-radical*-Theorie) in eindeutiger Weise. Im Fall eines schlechten Lösungsmittels spiegelt k_p eher die Änderung der lokalen Monomerkonzentration wider, die durch präferentielle Akkumulierung des Monomeren (als des besseren „Lösungsmittels") am Reaktionsort bedingt ist.

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Introduction

Polymerization in (homogeneous) solution can be considered to be the simplest extension of the so-called bulk polymerization. *i.e.* the polymerization of a pure monomer. It is no surprise, therefore, that the use of solvents during investigations of the kinetics of free radical polymerization dates already back about half a century. The mere establishment of the reaction order of the initial (overall) rate of polymerization with respect to monomer necessitates the variation of monomer concentration which is brought about by (partially) replacing the monomer by a hopefully inert solvent which does not take place in the reaction in any way and serves as a dummy for the monomer only. A nice example of such an investigation is given in Ref. [1] with respect to the polymerization of styrene in bromobenzene. This, however, cannot be regarded as a solvent effect according to the rules of chemical kinetics.

Without appearing explicitly, a solvent might act on each of the individual quantities in the equation of the rate for ideal free radical polymerization ν_p (except monomer and initiator concentration, $[M]$ and $[I]$, of course):

$$\nu_p = k_p k_t^{-1/2}[M][I]^{1/2}(2k_d f)^{1/2} \tag{1}$$

(k_p: rate of propagation, k_t: rate of (bimolecular) termination between growing chains, k_d: rate constant of first order decomposition of the initiator, f: initiator efficiency).

However, as long as rate measurements only are considered, $k_p(k_d f/k_t)^{1/2}$ cannot be resolved into its components and, thus, a solvent effect observed cannot be definitely attributed to one of the four quantities. There are indeed independent methods to study the solvent effect on k_d (in this case, k_d has to be measured as a function of the composition of the polymerization medium) or on f (here the rate of initiation $\nu_i = 2fk_d[I]$ has to be determined carefully in order to be in command of the product fk_d). All these procedures are standard material of the textbooks on free radical polymerization kinetics [1–3]. What is still left, however, is the separation of the solvent effect on k_p on the one hand and $k_t^{-1/2}$ on the other. This problem is equivalent to the problem of separating the combined expression $k_p k_t^{-1/2}$ into its individual components. For decades, this has been a very laborious task. The most promising and reliable procedure appeared to be rotating sector experiments, intermittently and periodically subjecting the system to photochemical initiation, measuring this pseudostationary rate of polymerization as a function of sector speed (a method which yields $k_p k_t^{-1}$), and combining this ratio with the ratio $k_p k_t^{-1/2}$ obtained from the analysis of stationary rate data according to Eq. (1).

Admittedly, the solvent effect on k_d and f is not very pronounced if certain precautions are met, *e.g.* an aliphatic azo compound is used as the initiator on the one hand and solvents of viscosity similar to that of the monomer on the other. The influence of the solvent on k_t is not fully straightforward. However, because the rate of bimolecular termination is considered to be controlled by diffusion, k_t should be inversely proportional to the viscosity of the medium (solvent+monomer).

In view of the huge efforts which are necessary for evaluating k_p as an individual constant – lacking a convenient and practicable method of directly determining k_p, and, in addition, deterred by the inevitable experimental scatter of individual k_p data – it is not surprising that generations of polymer kineticists preferred to investigate rates of polymerization in solution mostly neglecting solvent effects on f and k_d and, only occasionally, taking into account the influence of solvent viscosity on k_t [4–6], finally attributing the deviations from bulk polymerization to the action of solvent on the rate constant of propagation k_p.

Several theories were developed based on such rate measurements, some of them being already discussed in some detail by *Kamachi* [7]. Among those the most important ones are the theory of *Henrici-Olivé* and *Olivé* [8] on the one hand *Tüdös*' hot radical theory [9] on the other. In the first case it had been assumed that solvent as well as monomer may form electron donator-acceptor (EDA) complexes with the radical chains, the EDA complexes between radicals and monomer being exclusively responsible for the process of chain propagation. In this context, k_p values lower as well as higher than in bulk polymerization are reasonable depending on whether the solvent is the more effectful competitor in complex formation with the radicals than the monomer or not. In the hot radical theory it is argued that the heat of polymerization evolved in an individual propagation step is not removed instantaneously by collisions but is still partly contained in the radical for a certain (short) time, leaving a vibrationally excited hot radical. As long as such an excess energy is present, this will corroborate in acquiring the energy of activation necessary for the next propagation step. Because the average time between collisions which the radicals undergo with the monomer depends on monomer concentration, the probability of such a facilitated further propagation step clearly decreases with increasing solvent concentration (decreasing monomer concentration). As a consequence, k_p will be maximum in bulk polymerization, and any k_p observed in solution polymerization has to be smaller.

Both groups of workers have presented quite a number of data, each group claiming their data to be in support of the theory of their own: *Henrici-Olivé* and *Olivé* – mainly working with styrene as the monomer – found some systems where k_p was increased in comparison to bulk polymerization (bromobenzene and pyridine as the solvents); the majority of solvents, however, appeared to lower the propagation constant. Unfortunately, they did not represent their results in terms of k_p data so that a straightforward analysis is not quite easy. Nevertheless, according to their findings, k_p data should deviate significantly from the bulk values for 1:1 monomer/solvent mixtures. *Tüdös* and his group reported a lot of data, not only for styrene as the monomer but also for monomers of the acrylate type [10, 11], where for all solvents investigated k_p exhibited a more or less continuous decrease with dilution.

As already mentioned, all these results were based on rate measurements (Eq. (1)) or on k_p data derived from rotating sector measurements yielding k_p/k_t combined with k_p^2/k_t data from stationary measurements. About one decade ago, we succeeded in developing a rather convenient way of directly measuring k_p [12, 13]. This method, which is called the PLP-SEC method (Pulsed Laser Polymerization combined with a subsequent analysis of the chain-length distribution of the resulting polymer by Size Exclusion Chromatography), in the meantime has developed into a benchmark method of determining k_p and is successfully used throughout the world [14, 15]. It is a pseudostationary method (this means that the rate of initiation does not equal the rate of termination at every instant but only when averaged over a period as this is also the case with the classical rotating sector method) where periodic laser pulses are applied to a photopolymerizable system. When the next pulse arrives, those (few) radicals which have survived a period are suddenly opposed to a highly increased number of radicals, thus facing an increased probability of termination. As a result, the formation of dead polymer chains having a chain-length close to L_0 (or its multiple if the radicals had happened to survive not only one single full period) is favoured, this characteristic chain-length being connected with the propagation constant k_p and the time elapsing between two successive laser-pulses t_0 by the simple equation

$$L_0 = k_p \cdot [M] \cdot t_0 \tag{2}$$

In practice, L_0 is very well represented by the position of the point of inflection on the low-molecular-weight side of the peaks in the chain-length distribution which are associated with the preferential termination of the polymer radicals by the

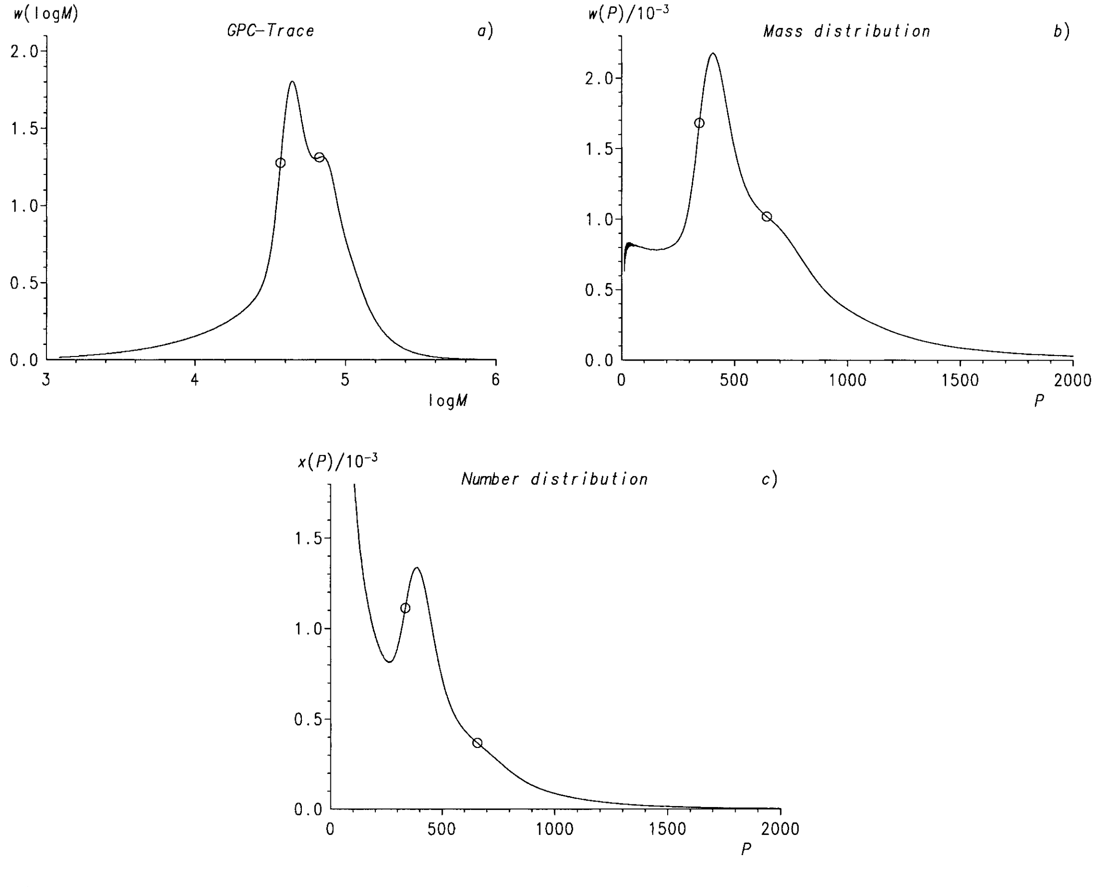

Fig. 1. Pulsed laser polymerization of styrene in bulk; time between two succesive laser pulses: $t_0 = 0.5$ s, monomer concentration: 8.65 $\text{mol} \cdot \text{l}^{-1}$, benzoin concentration: $5 \cdot 10^{-3}$ $\text{mol} \cdot \text{l}^{-1}$, temperature: $T = 25.0$°C, laser energy: $E = 40$ mJ/pulse; propagation constant k_p(k_p/$\text{l} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$) from the positions of the first points of inflection: of GPC-trace (a) $k_p = 81.9$, of mass distribution (b) $k_p = 80.0$, of number distribution (c) $k_p = 77.7$; from the postions of the second points of inflection: $k_p = 76.2$ (a), $k_p = 74.2$ (b), $k_p = 73.9$ (c), respectively

excess of (short) radicals produced in the next laser pulse. As an illustration of how this method works, three diagrams (Figs. 1a–c) are presented describing the system styrene in bulk at 25°C: the first one (a) is the original GPC trace which corresponds to a mass distribution $w(\log M)$ on a logarithmic molecular weight scale; the second one (b) gives the transformation of this curve into a conventional mass distribution with an abscissa linear in degree of polymerization, and the third one (c) finally illustrates the normal number chain-length distribution. The k_p values determined from the points of inflection (o) in these three types of distributions agree fairly well with each other and are also in good agreement with those – although less reliably – calculated from the second points of inflection depicting the situation after $2t_0$. With this method at our disposal, we decided to embark for a screening investigation of solution polymerization of the monomers styrene and methyl methacrylate in various solvents where always half of the monomer had been replaced by the solvent, thus reducing the monomer concentration to half of its bulk value. In addition, a 1:1 mixture of these two monomers was subjected to the same procedure, too, because the competition between these two monomers for complex formation, which can be of special importance, might be supposed to be projected in peculiar effects on the average k_p observed in such a solution copolymerization system.

Results and Discussion

The results are summarized in Table 1 for styrene polymerization, in Table 2 for polymerization of methyl methacrylate, and in Table 3 for the solution copolymerization styrene-methylmethacrylate 1:1. Apart from the k_p values, the tables contain the rate of polymerization v_p and the weight average degree of polymerization $\bar{P}_w$. The following solvents were used: Acetonitrile, dimethylformamide, toluene, anisole, methyl isobutyrate, bromobenzene, benzene, mesitylene, 1,2-dichloroethane, and cyclohexane, the latter in styrene-containing systems only. The polymerization was homogeneous in all cases.

Styrene

The effects of k_p were moderate throughout and only occasionally exceeded the limits of experimental error (estimated to be of the order of ±5%). Examples of this behaviour were acetonitrile (−12%), dimethyl formamide (*ca.* −12%), 1,2-dichloroethane (−10%), and cyclohexane (+20%). For all other solvents (toluene, anisole, methyl isobutyrate, bromobenzene, benzene, mesitylene) k_p did not differ significantly from its bulk value (*ca.* $80\,\mathrm{dm}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$). The large fraction which is made up of this type of solvents clearly contradicts the requirements of the hot radical theory where a general decrease of k_p should be observed. Contrary, also no convincing agreement with the theory of *Henrici-Olivé* and *Olivé* can be found, Mesitylene, which is clearly a solvent of high donating power (and therefore should efficiently compete with the monomer in complex formation), shows practically the same k_p as the bulk system, whereas dimethyl formamide, another donating solvent, indeed leads to some decrease of k_p. A special role is apparently played by cyclohexane which is known to be a θ-solvent for polystyrene at about

Table 1. Solution polymerization of styrene (50% v/v styrene, 25°C, $t_0 = 0.5$ s)

Solvent	k_p/l · mol^{-1} · s^{-1}	ν_p/10^{-5}l · mol^{-1} · s^{-1}	$\bar{P}_w$
acetonitrile	70.3	0.754	196.9
dimethyl formamide	67.6	1.215	158.8
dimethyl formamide	67.7	1.225	143.8
dimethyl formamide	70.4	1.533	126
dimethyl formamide	73.4	1.472	140
toluene	79.8	1.050	212.4
anisole	76.7	1.439	195.5
anisole	76.6	1.448	192.0
methyl isobutyrate	74.6	1.163	135.7
methyl isobutyrate	72.1	1.329	149
bromobenzene	72.7	1.823	120.9
bromobenzene	73.2	1.728	109.4
bromobenzene	74.9	1.517	180
bromobenzene	78.2	1.822	160
benzene	77.2	1.134	197.2
mesitylene	81.0	1.121	207.9
mesitylene	82.6	1.131	228.6
1,2-dichloroethane	72.4	1.101	237.0
1,2-dichloroethane	74.5	1.009	252.0
1,2-dichloroethane	75.3	1.008	245
1,2-dichloroethane	73.9	1.108	226
cyclohexane	94.6	2.996	258
cyclohexane	98.5	3.126	282
none	80	–	–

34°C. Of course, a 1:1 mixture of styrene and cyclohexane does not lead to polymer precipitation at 25°C; nevertheless, cyclohexane certainly is a bad solvent for the polystyrene formed. Because the quantity determined according to Eq. (2) rather is the product k_p $[M]$ (and not k_p itself) from which k_p usually is calculated by inserting the nominal overall monomer concentration $[M]$, the rather high value observed for k_p in this case may be interpreted as caused by an accumulation of the good solvent styrene (preferential solvation by monomer) in the vicinity of the radical chain ends, thus increasing the local monomer concentration beyond its nominal value.

Methyl methacrylate

The situation is rather similar to that encountered with styrene. Solvents like acetonitrile, anisole, bromobenzene, and mesitylene exhibit fairly the same k_p as observed in bulk polymerization. Systems containing methyl isobutyrate, benzene, toluene, and 1,2-dichloroethane are characterized by k_p values which are about 10% lower than in bulk. This is not quite consistent with the idea of the EDA-theory, as mesitylene is certainly a more powerful donating solvent than benzene and therefore should lead to a lower k_p in solution. The failure of the EDA concept in this case was already pointed out by *Burnett et al.* [16]. The observation that

Table 2. Solution polymerization of methyl methacrylate (50% v/v methyl methacrylate, 25°C, $t_0 = 0.5$ s)

Solvent	$k_p/\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$	$\nu_p/10^{-5}\,\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$	$\bar{P}_w$
acetonitrile	294.2	11.554	412.6
acetonitrile	296.4	11.517	400.4
dimethyl formamide	348.6	21.653	353.8
dimethyl formamide	340.9	21.635	395.6
dimethyl formamide	291.4	17.161	434
dimethyl formamide	303.0	16.701	502
toluene	274.4	13.017	353.4
toluene	264.0	14.305	318.8
anisole	294.2	18.290	385.3
anisole	291.5	20.101	385.9
methyl isobutyrate	259.9	13.470	284.2
methyl isobutyrate	255.3	13.898	273.0
methyl isobutyrate	254.8	16.752	242.8
methyl isobutyrate	261.8	18.959	282.0
bromobenzene	302.6	23.073	360.7
bromobenzene	306.1	22.658	373.0
benzene	267.0	14.338	320.0
benzene	265.0	11.813	341.0
mesitylene	288.9	17.335	300.1
mesitylene	281.9	17.911	325.2
1,2-dichloroethane	260.2	15.249	379
1,2-dichloroethane	267.3	13.773	485
1,2-dichloroethane	273.1	15.138	928
none	300	–	–

dimethyl formamide, which is rather considered to be a donating solvent, is the only one to show a k_p higher than that observed in bulk, points to the same direction. Of course, this would also contradict the hot radical theory which would admit lower k_p values in solution only. Admittedly, it should be mentioned that the heat of polymerization is comparatively small in the case of methyl methacrylate, thus reducing the chance of temporarily storing part of the heat of polymerization sufficient to facilitate the next propagation step.

Comonomer system styrene:methyl methacrylate

This system should be expected to behave rather like pure styrene for two reasons: firstly, the average k_p in this system is very similar to that observed in pure styrene [17]; secondly, this copolymerization system is nearly an azeotropic one leading to a copolymer which has a composition very close to the composition of the comonomer system (1:1). Because k_p for radicals ending in methyl methacrylate units is nearly four times that for radicals ending in styrene units, the overall population of radicals is governed by the latter ones (75–85%, depending on the model applied) [17]. This expectation is also widely reflected in the k_p data

Table 3. Solution copolymerization of styrene and methyl methacrylate 1:1 (50% v/v monomers 25°C, $t_0 = 0.5$ s)

Solvent	$k_p/\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$	$\nu_p/10^{-5}\,\mathrm{l \cdot mol^{-1} \cdot s^{-1}}$	$\bar{P}_w$
acetonitrile	87.4	1.226	143.2
acetonitrile	86.6	1.251	127.5
dimethyl formamide	89.3	2.185	126.6
dimethyl formamide	97.2	2.516	117.0
dimethyl formamide	95.8	2.459	125.6
toluene	79.5		113.1
toluene	78.7	1.588	116.1
anisole	83.5	1.705	143.0
anisole	85.0	1.843	134.2
methyl isobutyrate	76.3	1.442	89.8
methyl isobutyrate	78.0		86.6
methyl isobutyrate	81.6	1.7996	90
methyl isobutyrate	85.5	1.815	99
bromobenzene	80.4	2.341	126.8
bromobenzene	78.6	2.339	122.5
bromobenzene	87.1	2.193	146.3
bromobenzene	86.9	2.277	125.0
benzene	78.7	1.530	107.7
benzene	78.6	1.446	108.7
mesitylene	81.5	1.328	123.8
mesitylene	82.5	1.647	130.2
1,2-dichloroethane	82.8	1.844	173
1,2-dichloroethane	83.2	1.896	154
cyclohexane	103.9	1.507	116
cyclohexane	100.5	1.524	128.7
none	81.9	–	–

observed: toluene, anisole, methyl isobutyrate, bromobenzene, benzene, mesitylene, and 1,2-dichloroethane as solvents are of negligible influence on k_p, whereas slightly increased k_p values (somehow in contradiction to the results obtained for styrene polymerization) are observed for acetonitrile and dimethyl formamide as solvents. The only marked increase is observed for cyclohexane – in accordance with the observations for styrene polymerization. For a 1:1 copolymer cyclohexane again is a bad solvent which makes it plausible that monomer (styrene as well as methyl methacrylate) as a good solvent is preferentially accumulated in the vicinity of the growing radicals, thus pretending an increased value of k_p. In all, no specific effects arising from a competition between the two monomers (relative to the solvent) appear to be present.

Conclusions

On the whole, the data collected do not favour one of the two theories on solution polymerization over the other. Rather there is a disagreement with either of them –

at least in some qualitative respects. With respect to quantitative aspects it can be said that the influence of solvent on k_p in these systems containing half the bulk monomer concentration is weaker than supposed earlier. The observations made with the non-solvent cyclohexane, in addition suggest that – at least in those systems, where no specific interactions are present – the product $k_p[M]$, as determined according to Eq. (2), rather reflects changes in the local monomer concentration at the site of reaction than changes in the reactivity of radicals induced by the presence of solvents. Of course, this does not necessarily exclude the occasional existence of specific effects such as those reported by *Davis et al.* for N-methyl pyrrolidone in styrene polymerization [18] or those reported as well by *Davis et al.* [18] and by *O'Driscoll et al.* [19] for benzyl alcohol in styrene and methyl methacrylate polymerization where a substantial increase of k_p in comparison to bulk polymerization was observed. Apart from these specific effects, our results convey the impression that there is a slight tendency that k_p in solution is a little smaller than in bulk. This would be in some qualitative accordance with the hot radical theory, however, without providing any proof. Anyway, an extension of this type of screening investigation to other monomers, especially those characterized by high values of k_p and high heats of polymerization (such as acrylates), might cast some light on the problems encountered.

Experimental

Laser

An excimer laser (Lamda Physik, EMG 101) operated at 351 nm (XeF) was used as a periodic light source. According to the specifications of the instrument, the energy per pulse was close to 100 mJ with a pulse width of 14 ns at an amplitude stability of ±3%.

Materials

The monomers (styrene and methyl methacrylate, both reagent grade) were distilled in a nitrogen atmosphere under reduced pressure (under slightly reduced pressure in the case of methyl methacrylate). Benzoin (reagent grade) was used after recrystallization. All solvents were reagent grade and had been distilled under nitrogen before use.

Polymerizations

Reactions were carried out in a thermostat kept at 25°C in a vacuum-tight quartz cells with an optical cross section of $4\,\text{cm}\times 1\,\text{cm}$ or $3\,\text{cm}\times 1\,\text{cm}$, respectively; $3\,\text{cm}^3$ monomer/solvent/sensitizer (benzoin at $4\cdot 10^{-3}\,\text{mol}\cdot\text{l}^{-1}$) mixtures were degassed by freeze-thaw cycles at the high vacuum line, and finally sealed. The conversion was kept as low as possible (usually below 2.5%).

Size exclusion chromatography

Before dissolving the polymers in *THF* (mass fraction of polymer ≤ 0.0025) for SEC analysis, the monomer(s) were removed under vacuum, and the sample was subjected to freeze-drying until constant weight was obtained. Four Waters μ-styragel columns (500 Å, 10^3 Å, 10^4 Å, and 10^5 Å) were used at room temperature. A Pye Unicam LC-UV detector (wave length 270 nm for styrene-containing polymers und 235 nm for poly(methyl methacrylate)) was employed, and the data were recorded and transformed by a Spectra-Physics computing integrator SP 4100. Eight standards with narrow molecular weight distribution (polystyrene and poly(methyl methacrylate), respectively) were used for the construction of the calibration curves for the analysis of polystyrene and poly(methyl methacrylate) samples; for the poly-co(styrene-methyl methacrylate), a calibration curve was calculated based on a linear combination of the calibration curves for polystyrene and poly(methyl methacrylate) as in Ref. [17]. The molecular weight distribution curves were finally analysed for their points of inflection by numeric differentiation and looking for the position of the maximum of the first derivative.

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