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REVIEW

Gradient copolymers

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Abstract Gradient copolymers represent a relative new class of copolymers containing at least one section of the macromolecule where the chemical composition continuously changes along the polymer chain. Due to their structural relation to block copolymers, microphase-segregated structures can be formed in bulk, in solution, at surfaces, and interfaces exhibiting a blurred, less-defined border region between phases. The article reviews the preparation methods, the main physical peculiarities, and some proposed applications of gradient copolymers.

Keywords Gradient copolymer · Gradient block copolymer · Definition · Preparation · Properties · Application

Definition

Linear block copolymers are made from polymer chains of different chemical composition that are covalently joined via their respective end groups [1]. This classical architecture of block copolymers implies an abrupt change in composition at the connection point of the adjacent blocks (cf. Scheme 1a). However, during the last decade, a new type of copolymer came to the focus of scientific interest with its chemical composition claimed to vary continuously along a certain section of the polymer chain. Macromolecules that contain at least one section of continuously changing monomer composition are called 'gradient polymers' or 'gradient copolymers' (Scheme 1b) [2, 3]. Earlier review articles on the field can be found in references [4–6].

The term must not be mixed up with (semi)interpenetrating networks that contain macroscopic structural or compositional gradients along the spatial position of the sample, although such materials, investigated since the early 1970s, have also been called 'gradient polymers' [e.g., 7, 8].

Prior to the discussion of synthesis, properties, and possible applications of gradient copolymers, it is worthwhile to consider the definition of the term 'continuous change in monomer composition'. Figure 1a schematically depicts the most frequently used plot of the local polymer composition $F_1(X)$ against the degree of polymerization X, implying the continuous change in monomer composition along the polymer chain. In this graph, the local compositional gradient $g(X)$ is defined as the first derivative of the composition with respect to the degree of polymerization (Eq. (1)).

$$g(X) = \frac{\mathrm{d}F_1(X)}{\mathrm{d}X} \tag{1}$$

($g(X)$=local compositional gradient, F_1=molar fraction of monomer 1 in the copolymer, X=degree of polymerization)

The definition of Eq. (1) presumes that the local monomer composition $F_1(X)$ of an individual macromolecule is a continuous function in X. This is, however, not the case, because monomer units are of discrete nature: One cannot incorporate 1/2, or 1/8 of a monomer unit at a specific position. The true situation is sketched in Fig. 1b, showing an example sequence of 20 monomer units. Although the composition of this model chain varies from $F_1(X=1)=1.0$ to $F_1(X_e=20)=0$ (with the average composition of the chain $<F_1>=1/2$), it is not possible to assign an unambiguous value of the compositional gradient. The calculus of discrete functions replaces the differential quotient of Eq. (1) against difference quotients and allows to

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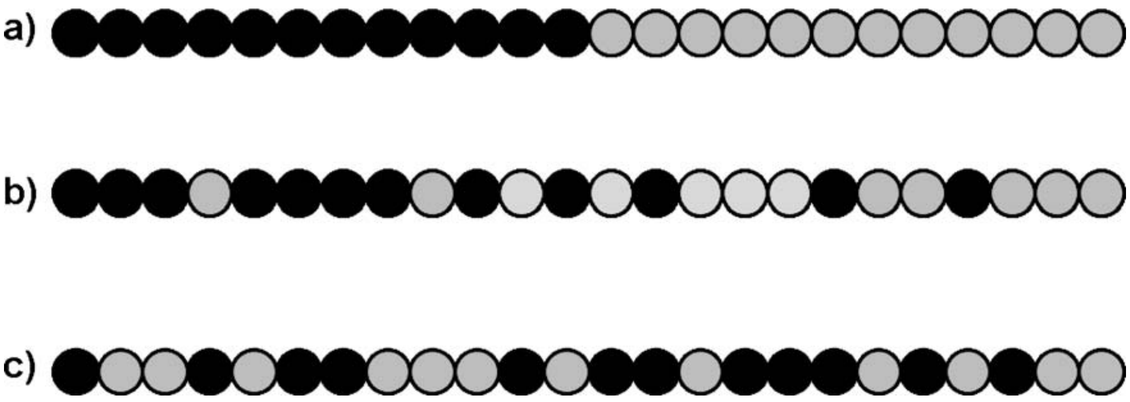

Scheme 1 Schematic depiction of the monomer sequences in a diblock copolymer P[A]-*b*-P[B] (**a**), a gradient copolymer P[A-*grad*-B] (**b**), and a random copolymer P[A-*co*-B] (**c**) of equal composition (50 mol% A)

define three values of the local gradient, namely the 'forward' ($g_\mathrm{f} = [F_1(X{+}\Delta X) - F_1(X)]/\Delta X$), the 'backward' ($g_\mathrm{b} = [F_1(X) - F_1(X - \Delta X)]/\Delta X$) and the 'central' difference quotient ($g_\mathrm{c} = [F_1(X{+}\Delta X) - F_1(X - \Delta X)]/(2{\cdot}\Delta X)$) [9]. If one agrees to use one of these difference quotients as the standard definition of the 'gradient' the result becomes counter intuitive. Applied to e.g., position X=10 of our model chain and using ΔX=1 one finds the values $g_\mathrm{f}(10)$=+1, $g_\mathrm{b}(10)$=−1, and $g_\mathrm{c}(10)$=0, respectively. It seems to be a loophole to use the compositional average over *n* positions around a given place *X* as basis to calculate the gradient. Such a definition comes down with two new problems. First, the number *n* remains arbitrary and second, *n* must be comparable to the block length X_e to approach the value of the gradient. In any case, the compositional gradient of an individual copolymer chain cannot unambiguously be defined.

$$\left\langle F_1^{(\mathrm{loc})}(X)\right\rangle = \frac{1}{N}\cdot\sum_{i=1}^{N} F_{1,i}(X) \tag{2}$$

($\left\langle F_1^{(\mathrm{loc})}(X)\right\rangle$=ensemble average of the local chain composition, $F_{1,i}(X)$=composition of polymer chain *i* at position *X*, *X*=degree of polymerization, *N*=number of polymer chains in the sample)

If a property cannot be assigned to an individual molecule, one has to use ensemble averages. Equation (2) defines the ensemble average of the local composition $\left(\left\langle F_1^{(\mathrm{loc})}(X)\right\rangle\right)$ as the average over the composition of all present polymer chains at a given position *X*. This value is well defined, continuous and related to experimental data obtained from macroscopic amounts of a polymer. Because of these properties, Eq. (1) can be applied and Fig. 1a becomes valid.

However, one has to bear in mind that the composition of almost any individual molecule will distinctly deviate from this average value, because even highly precise synthetic procedures generate chain composition distributions [10].

In case that the compositional gradient is of the same value along the whole gradient section, the polymer is called 'linear gradient' or 'constant gradient' polymer. Note that the first term may cause confusion when used in connection with macromolecules of non-linear architecture (e.g., brush, branched, hyperbranched, or dendritic polymers).

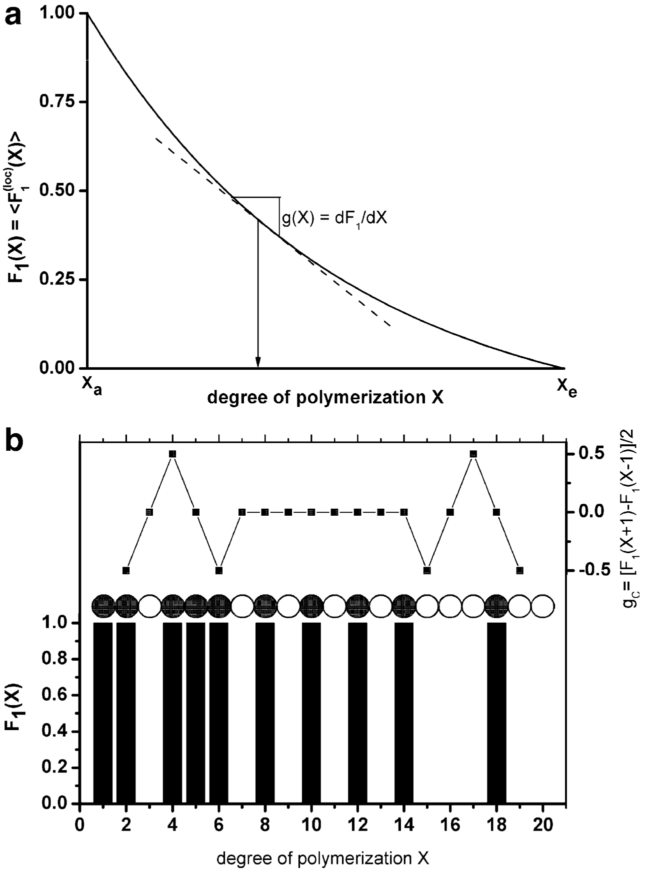

Fig. 1 **a** Depiction of a continuous change of composition along a polymer chain with the definition of a compositional gradient and **b** illustration of the problem to define a local gradient in a single macromolecule

Preparation of gradient copolymers

Consider the task to prepare a gradient block of the general structure $P[M_1\text{-}grad\text{-}M_2]_{X_e}$ with X_e denoting its degree of polymerization. Along the gradient block the polymer composition should continuously change from $F_1=F_{10}$ at the start of this block down to $F_1=F_{1e}$ ($F_{1e}<F_{10}$) at its very end.

With a given pair of monomers the relative rate of incorporation of a monomer unit in the growing polymer chain is exclusively determined by the monomer composition of the reaction mixture (terminal model, Lewis–Mayo equation, Eq. (3)) [11]:

$$F_1=\frac{d[M_1]/dt}{d[M_2]/dt}=\frac{r_1\cdot f_1^2+f_1\cdot f_2}{r_1\cdot f_1^2+2\cdot f_1\cdot f_2+r_2\cdot f_2^2} \tag{3}$$

(F_1=local molar fraction of monomer 1 in the polymer, f_1= molar fraction of monomer 1 in the reaction mixture, $f_2=1-f_1$, r_1, r_2=copolymerization parameter)

The first condition to prepare a gradient block is obviously to use a polymerization technique that does not include termination reactions. In a conventional free radical polymerization where the lifetime of an individual radical (0.1–10 s [12]) is negligible against the reaction time, any change of the reaction mixture composition with time will result in a mixture of macromolecules differing in monomer composition. It is characteristic for either living or even controlled polymerization reactions that the growing species do not terminate during the reaction [13]. Hence, the variation of the monomer composition of the reaction mixture is mapped by means of Eq. (3) (or another copolymerization equation) onto the growing polymer chain.

Since in principle all living or controlled polymerizations can be applied to prepare gradient copolymers, it has been reported that anionic polymerizations [14–17], cationic polymerizations [18, 20, 21], ring-opening metathesis polymerizations (ROMP) [22] as well as controlled radical polymerization techniques [23] like nitroxide-mediated polymerization (NMP) [24–32], radical addition fragmentation and transfer (RAFT) [33–35], and atom transfer radical polymerization (ATRP) [6, 36–43] can be used.

Not only gradient polymers can be produced, but also the synthesis of block-gradient, graft-gradient, and block-graft-gradient polymers has been reported [36, 44, 45]. Table 1 gives a non-exhaustive overview over published gradient polymer preparations.

Two distinctly different experimental approaches can be distinguished to control the compositional gradient, namely the 'spontaneous'- and the 'forced'-gradient methods.

Spontaneous gradient polymerizations are batch-copolymerization reactions where a monomer mixture is polymerized to high conversions [38, 46]. In the absence of either azeotropic points or ideal random copolymerizations, the monomer composition will change gradually with the monomer conversion because of the different reactivity of the monomers. As determined by Skeist's equation [47], a typically non-constant compositional gradient evolves along the polymer chain.

The majority of gradient copolymers reported so far have been made in this way, even surface induced polymerizations to generate gradient polymer modified aluminum oxide particles have been performed [48].

The spontaneous gradient technique is quite a simple experimental method but suffers from three drawbacks: It is only applicable to strictly non-random copolymerization systems and will fail in close vicinity to azeotropic points; it cannot be used to cross the full compositional space from $F_{10}=1$ to $F_{1e}=0$ (one can obviously not start with a single monomer) and it is virtually impossible to generate constant compositional gradients over the full range of monomer composition.

'Forced' gradient copolymerizations are semi-batch reactions involving the initiation of a polymerization in a pure monomer or a monomer mixture and the subsequent continuous addition of monomers—or a monomer mixture—during the reaction time [49]. The addition rates as well as the composition of the added mixture may be varied and allow for full control on the composition of the generated copolymer chain. Gradient copolymers, as well as block copolymers of the structure containing arbitrary compositional gradients with composition ranges within the gradient block from $F_{10}=1$ to $F_{1e}=0$ can only be prepared by means of forced gradient techniques [50].

In case that the composition of the reaction mixture as well as the polymer composition can continuously be measured during the experiment, an iterative procedure has been proposed to generate constant gradient copolymers [49]. A setup of a model-free 'automatic continuous on-line monitoring of polymerization reactions' system (ACOMP) was reported and used for the production of constant gradient styrene/*n*-butyl acrylate polymers by means of NMP [24]. The ACOMP system continuously extracted a small stream of the reaction solution, diluted with solvent, and fed it in a series of detectors (multi-angle light scattering, viscosity, refractive index, and UV/Vis detector) to determine the required reaction mixture and polymer composition. The analytic data were used to adjust the monomer feed accordingly to generate perfect constant gradient copolymers [24] (Fig. 2a).

When lacking the equipment for continuous on-line measurement of the monomer- and copolymer composition, experimentalists applied 'blind flight' strategies, involving the addition of monomer to a reaction mixture, aliquot taking and off-line analysis of the samples. By means of this strategy, one obtains post-reaction information on the prepared polymers

Table 1 Examples of published gradient and block-gradient copolymer syntheses

Polymer	Method	Tech.	Ref.
P[Sty-*grad*-MA]	ATRP	S, F	[2]
	NMP	S	[29]
P[Sty-*grad*-4-AcetoxySty]	NMP	F	[31]
P[Sty-*grad*-4-HydroxySty]			[31]
P[Sty-*grad*-*n*-BuA]	ATRP	S, F	[3, 6]
	NMP	S	[65]
	NMP	F	[28]
	RAFT	F	[23, 56]
P[Sty-*grad*-AN]	ATRP	S, F	[51]
P[MMA-*grad*-MA]	ATRP	S	[2]
	ATRP	F	[55]
P[MMA-*grad*-*n*-BuA]	ATRP	S	[6, 47]
	RAFT	S	[33]
P[MMA-*grad*-VCl]	ATRP	F	[55]
P[MMA-*grad*-(BPEM-*graft*-*n*-BuA)]	ATRP	S	[43]
P[MMA-*grad*-PDMS-MA]	ATRP	S	[44]
P[ODA-*grad*-*t*-BuMA]	ATRP	S	[40]
P[ODMA-*grad*-*t*-BuA]	ATRP	S	[40]
P[ODA-*grad*-MMA]	NMP	S	[30]
P[n-BuMA-*grad*-*t*-BuMA]	ATRP	F	[57]
P[n-BuMA-*grad*-MAA]			[57]
P[HEA-TMS-*grad*-MMA]	ATRP	S	[67]
P[(BDEM-*graft*-BuA)-*grad*-BuA]			[67]
P[HEA-TMS-*grad*-BuA]	ATRP	S	[67]
P[(BDE-*graft*-BuA)-*grad*-MMA]			[67]
MPEG-*b*-P[DMAEMA-*grad*-BuMA]	ATRP	S	[41]
MPEG-*b*-P[BuMA-*grad*-DMAEMA]	ATRP	S	[41]
P[BuA]-*b*-P[MMA-*grad*-BuA]	ATRP	S	[35]
P[CHTS-*grad*-functional trisiloxane]	LAn	S	[15, 16]
P[EOVE-*grad*-MOVE]	LCat	S	[75]
P[MOX-*grad*-POX]	LCat	S	[76]
P[MOX-*grad*-NOX]	LCat	S	[78]
P[BuBONB-*grad*-BONB]	ROMP	F	[21]

Methods: *ATRP* atom transfer radical polymerization, *NMP* nitroxide-mediated polymerization, *RAFT* radical addition fragmentation and transfer, *LCat* living cationic polymerization, *LAn* living anionic polymerization

Techniques: *S* spontaneous gradient, *F* forced gradient

Monomers: *AN* acrylonitrile, *BONB* benzyloxynorbornene, *BuBONB* butylbenzyloxynorbornene, *BPEM* 2-bromo-isopropyloxy-ethyl methacrylate, *BuA* butylacrylate, *CHTS* cyclohexyltrisiloxane, *EOVE* ethoxyvinylether, *HEA-TMS* trimethylsilyloxy-ethyl methacrylate, *MA* methyl acrylate, *MAA* methacrylic acid, *MOVE* methoxyvinylether, *MOX* methyl-2-oxazoline, *NOX* nonyl-2-oxazoline, *PDMS-MA* polydimethylsiloxane mono methacrylate, *ODA* octydecylacrylate, *ODMA* octadecylmethacrylate, *POX* 2-phenyl-2-oxazoline, *Sty* styrene, *VCl* vinyl chloride

composition. Successful experimental attempts have been reported to create gradient copolymers by continuous addition of monomers at constant addition rate [2, 3, 51].

The first published example was the forced gradient copolymerization of styrene and methyl acrylate by means of ATRP [2]. It was found that increasing rates of acrylate addition to styrene changed the obtained gradient from a blocky structure to a fairly constant gradient copolymer (cf. Fig. 2b). Similar observation was made with styrene and *n*-butyl acrylate (ATRP) [3], styrene/4-acetoxy-styrene and styrene/4-hydroxystyrene (nitroxide mediated) [22]. When, however, the comonomer pair styrene/acrylonitrile (AN) was subjected to a forced gradient treatment with addition of AN to styrene, the more constant gradient was obtained with small addition rates [52] (see Fig. 2c).

Since the compositional gradient not only depends on the monomer reactivity ratios but also on the ratio of monomer addition rate to rate of polymerization, no simple rule of thumb can be given that states if either slow or fast monomer addition may guarantee fairly constant gradients.

A more complex experiment was reported with 5-substituted norbornenes (monomer 1=*exo*-5-(benzyloxy) norbornene, monomer 2=*exo*-5-[(4-*tert*-butyl)benzyloxy] norbornene) that were ROMP copolymerized by means of a Grubbs type catalyst. The authors compared the effect of feeding either one monomer or both the monomers at constant

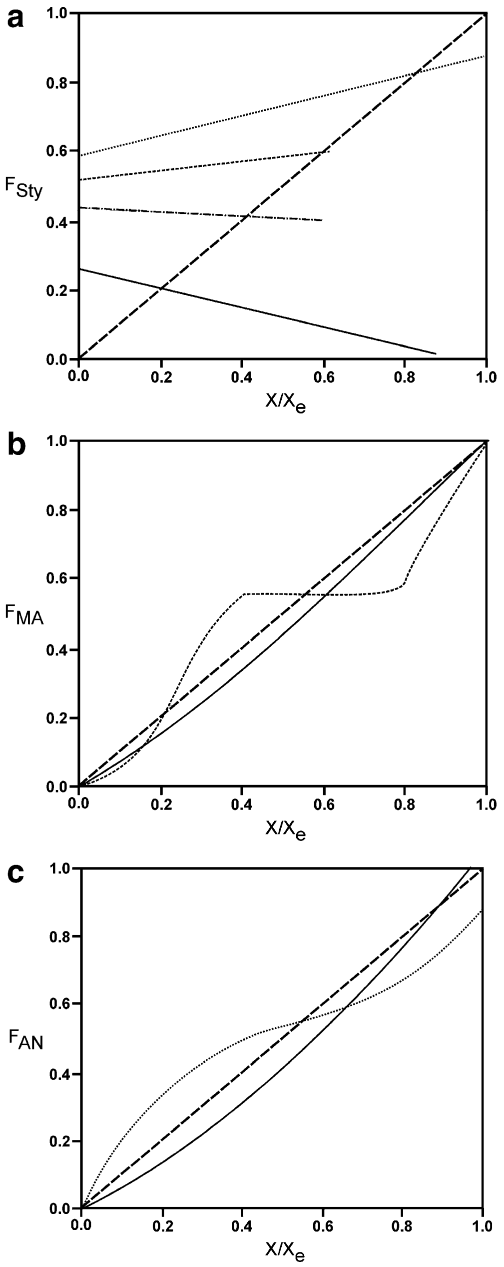

Fig. 2 Local composition of forced gradient copolymers. **a** *n*-Butyl acrylate/styrene, automated feedback-loop-controlled monomer addition (····=70/30, —=50/50, -·-·-=30/70, —=10/90 initial molar ratio styrene/butyl acrylate) [24], **b** methyl acrylate/styrene, constant rate addition of methyl acrylate (—=slow addition, —=fast addition, - - -=$1-X/X_e$) [3], **c** acrylonitrile/styrene, constant rate addition of acrylonitrile (——=slow addition, —=fast addition) [52]. Re-drawn with data from [3, 24, 52]

addition rates and stated that the 'dual ramp strategy' (i.e., feeding both the monomers independently) offered a more extensive control over the course of the gradient. In particular, at larger conversions (>70%), deviations from the constant gradient structure could be reduced [22].

Theories have been developed to predict complex time-dependent monomer addition schemes, adapted to the respective copolymerization kinetics to guarantee the generation of pre-defined gradients by means of 'blind flight' semi-batch experiments.

In case that an arbitrary gradient function $g(X)$ shall be realized, one has to solve the differential equation system (DES) (Eqs. (4) and (5)) to calculate the amount of monomer to be added at a certain monomer conversion p [50].

$$\frac{dq}{dp} = \frac{X_e \cdot g(X)}{F_1'} \cdot \frac{q-p}{\alpha_1 - f_1} + \frac{F_1 - f_1}{\alpha_1 - f_1} \qquad (4)$$

$$\frac{df_1}{dp} = \frac{1}{q-p} \cdot \left\{ f_1 - F_1 + \frac{dq}{dp} \cdot (\alpha_1 - f_1) \right\} \qquad (5)$$

($g(X)$=targeted copolymer compositional gradient, X_e= targeted length of the gradient block, $F_1'=dF_1/df_1$, q=total monomer addition function, α_1=molar fraction of monomer 1 in added monomer mixture, p=monomer conversion, F_1= instantaneous molar fraction of monomer 1 in the copolymer, f_1=instantaneous molar fraction of monomer 1 in the monomer mixture).

To make the scheme work, the time dependency of the monomer conversion, as well as the required monomer addition is needed. Systematic presentations of how to calculate the required polymerization/monomer addition programs are scarce, although for free radical copolymerizations an extensive amount of literature dealing with the control of copolymer compositions with batch, semi-batch, or continuous reactor systems still exists (for review, see [53, 54]). It is, however, the main goal of free radical composition control to avoid any change of monomer and copolymer composition during the course of the reaction to impede the formation of mixtures of compositional varying copolymers.

A most complete mathematical model of RAFT and ATRP semi-batch polymerization kinetics has been proposed, taking into account kinetic equations for each type of chain species such as radicals, dormant, and dead end polymers [55]. This model allowed to predict the time evolution of monomer conversion, molecular weight, and polydispersity of the gradient copolymer. The model was used to derive monomer addition programs for the comonomer pairs styrene/*n*-butyl acrylate, methyl methacrylate/methyl acrylate, and methyl methacrylate/vinyl chloride. The programs were experimentally proven to enable a high degree of control over the compositional gradient of the respective copolymers [56, 57].

The complete description of polymerization mechanisms requires a large number of kinetic parameters that may sometimes be cumbersome to retrieve. For this reason, a simplified 'phenomenological' approach has been proposed [50] that replaces the details by an empiric 'gross' kinetic function (cf. Eq. (6)), and extends the DES (Eqs. (3) and (4)) to predict the conversion/time relation. Note that

Eq. (5) is an approximation that does not take into account the volume contraction of the solution due to polymerization.

$$\frac{dt}{dp} = \frac{1 + \gamma \cdot (q - q_0)}{\kappa(f_1) \cdot [I]_0 \cdot (q - p)} \tag{6}$$

(p=monomer conversion, t=reaction time, $\kappa(f_1)\cdot[I]_0$= effective kinetic rate constant, f_1=molar fraction of monomer 1 in the solution, q=monomer addition function, γ= dilution factor due to monomer addition).

The required parameter function to control a specific binary copolymer system, $\kappa(f_1)$, can be collected by means of a low number of pilot polymerizations. The scheme makes a compromise between the full theory or full equipment-based ‘perfect control procedures’ on one hand and the ‘try and error’ constant rate addition programs on the other hand.

The procedure was tested with the ATRP copolymerization of the almost ideal randomly copolymerizing pair *n*-butyl methacrylate/*t*-butyl methacrylate to yield satisfying control up to monomer conversions of 74–87% [58], although the dilution effect was not taken into account (Eq. (5); γ=0).

Properties of gradient copolymers

Since it became early possible to calculate the chain statistics of gradient copolymers [59, 60], it has been predicted that the thermal properties as well as the bulk structures of such ‘gradient’ copolymers should deviate from that of statistical or diblock copolymers. Gradient copolymers were calculated to undergo microphase separation like block copolymers and should form lamellar structures in the symmetric case (cf. Fig. 3), but the interface region between the chemically different regions will be blurred [61]. Recent theoretical developments indicated that the lamellar phase may be the only stable microphase-segregated state of gradient copolymers [62]. Gradient copolymers may offer a large degree of control over the A–B interfacial profile [63, 64] and the extent of their microphase segregation should depend on the actual shape of the gradient [63].

Experimental investigations showed quenched styrene/butyl acrylate gradient copolymer melts [65, 66] to exhibit a very broad glass transition located between the glass temperatures of the respective homopolymers, and the same has been reported with styrene/4-acetoxystyrene [32] and methyl methacrylate/polydimethylsiloxane mono methacrylate gradient copolymers [67]. Furthermore, broad relaxation time distributions, as measured by means of melt rheology, indicated the presence of the expected phase segregated structures with blurred inter-phase regions (cf. Fig. 4) [65, 67]. The preparation of brush-type gradient copolymers composed of a (meth)acrylate backbone and a gradient distribution of polydimethylsiloxane side chains allowed to

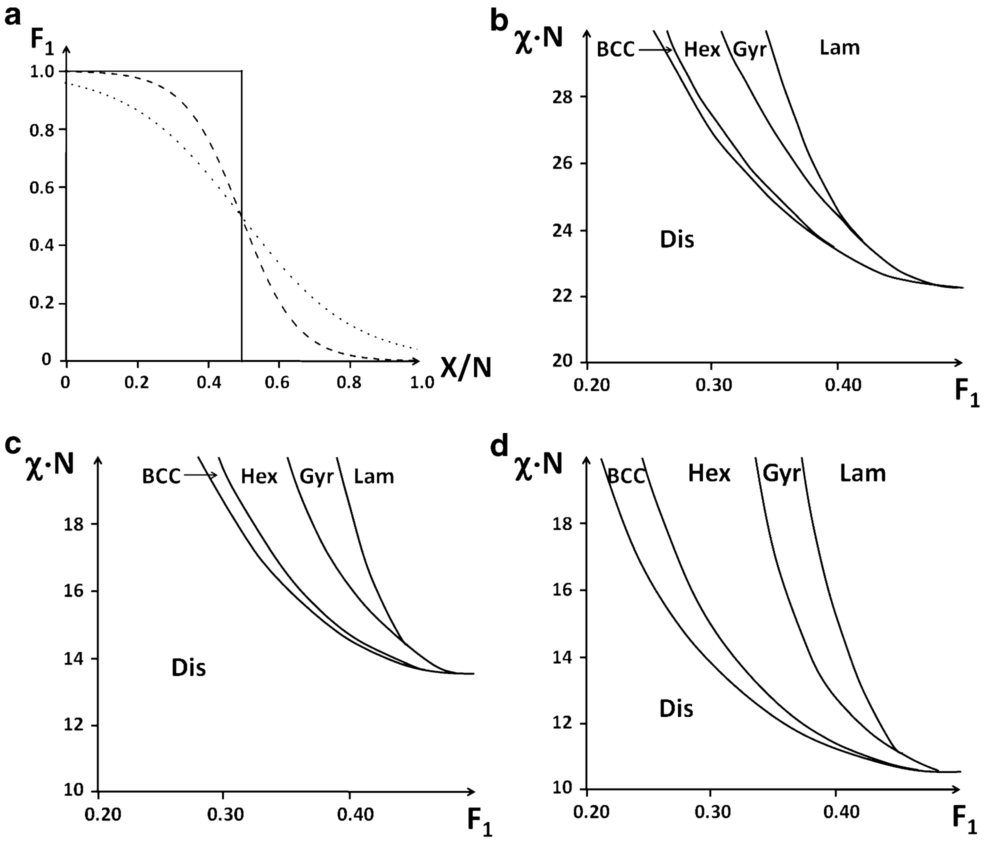

Fig. 3 Self-consistent mean field calculations of the phase behavior of gradient and block copolymers. **a** Monomer distribution along the polymer chains: ·····=‘flat gradient’, —=‘steep gradient’, —=block copolymer, **b** phase diagram of the ‘flat gradient’ copolymer, **c** the ‘steep gradient’ copolymer, and **d** the block copolymer. *BCC* body centered cubic, *Hex* hexagonal, *Gyr* gyroid cubic, *Lam* lamellar, *Dis* disordered phase. F_1 molar fraction of monomer 1, X/N relative position along the polymer chain, N degree of polymerization, χ Flory Huggins interaction parameter between monomer unit types 1 and 2. Redrawn with data from [62]

visualize the gradient structure by means of scanning force microscopy [44, 68]. The Young modulus of these gradient copolymers was close to that of the random copolymer of comparable composition; however, the gradient copolymer was tougher then the random copolymer [67].

Recent studies on styrene/4-acetoxystyrene as well as styrene/*n*-butyl acrylate gradient copolymers by means of rheology and small-angle X-ray scattering studies supported the general tendencies of the gradient polymers to exhibit broadened/blurred phase transitions. Depending on molecular parameters such as (1) molecular weight, (2) gradient structure, and (3) segregation tendencies, as expressed by the $\chi_{12} \cdot N$ parameter (χ_{12}=Flory Huggins parameter between polymer units of type 1 and 2, N= degree of polymerization of the block or gradient polymer), the transition behavior can be controlled. In particular, in the weak segregation regime (low molecular weight or low mutual incompatibility), the phase behavior becomes complicated, but, however, offers new opportunities to design materials properties [69].

Gradient copolymers from octadecylacrylate and methyl acrylate exhibited considerably lower melting temperatures ($\Delta T = -10$ °C) than block copolymers made from the same monomers. Since the melting temperature range was simultaneously broadened by a factor of 2–3, the interruption of crystalline octadecylacrylate sequences by amorphous chain regions was deduced [31].

At interfaces, gradient copolymers were calculated to form Alexander brushes even with weak segregation tendencies between the constituent units, as long as one chain end becomes fixed to the surface [70]. Without this restriction, i.e., when considering an interface between immiscible P[A] and P[B] polymers, the P[A-*grad*-B] gradient polymer should enrich at the interface, but the concentration profile should be less narrow as compared to a block copolymer P[A]-*b*-P[B] (cf. Fig. 5) [63].

The interfacial activity of random, block, and gradient copolymers from *exo*-5-(benzyloxy)norbornene and *exo*-5-(4-*t*-butyl-benzyloxy)norbornene has experimentally been investigated [71] and found to obey previous theoretical considerations [63]: Upon mixing with the benzyloxy-norbornene homopolymer, the block copolymer formed a monolayer with low-energy surface, i.e., the *t*-butyl units segregated towards the solid/air interface, while the gradient copolymer ($g(X)$=1) built low-energy surface interlayers that were broader than that of the block copolymer (Fig. 5).

Micelle formation is observed with block copolymers in solvents that selectively dissolve one of the blocks [72, 73]. Up until now, the number of investigations on gradient copolymer solution structures is limited, but theory demands gradient copolymers to exhibit larger values of the critical micelle concentration than block copolymers [63]. In poly methyl methacrylate as the solvent, styrene/methyl methacrylate gradient copolymers exhibit critical micelle concentrations that are about ten times larger than that of respective PS-*b*-PMMA block copolymers [74], in qualitative accordance to the prediction.

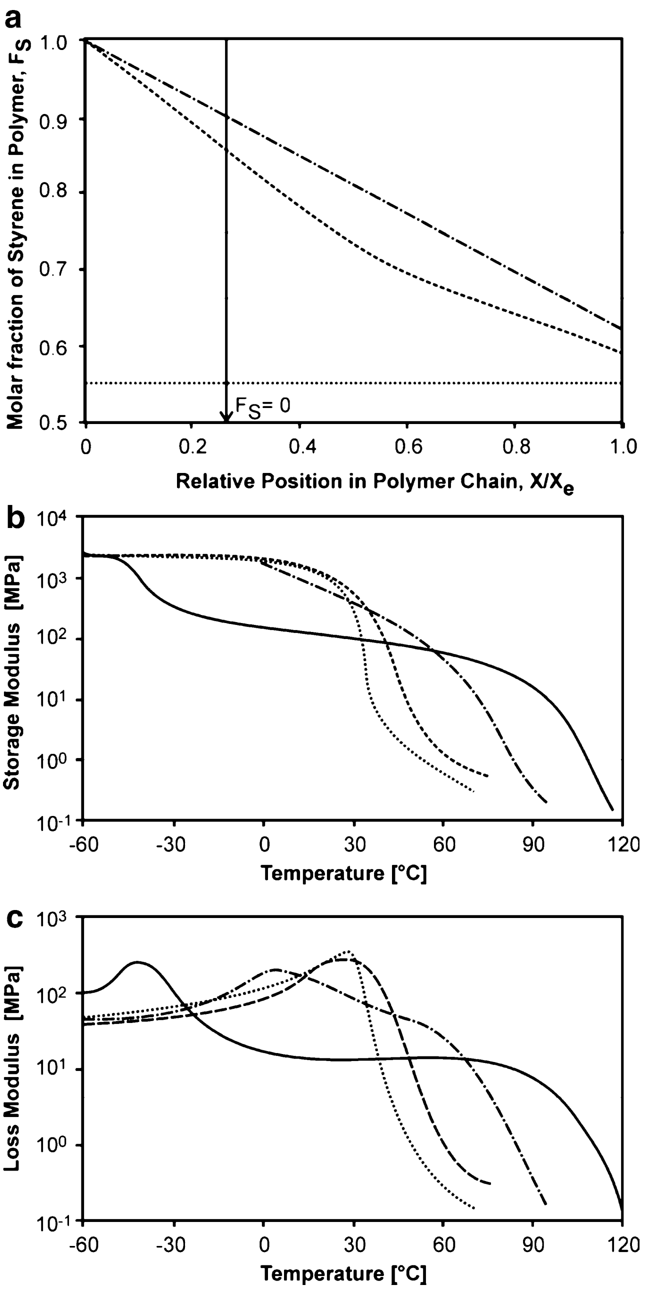

Fig. 4 Dependence of the monomer distribution along the polymer chain and effect of the monomer sequence on **a** the storage modulus and **b** on the loss modulus **c** of styrene/*n*-butyl acrylate block (—), gradient (-·-·- and —), and random copolymers (·····). Re-drawn with data from [87]

Micelle formation in aqueous solution as supported by ^{1}H NMR spectroscopy was observed with methoxypoly-ethyleneglycol-*b*-poly[dimethylaminoethyl methacrylate-*grad*-*n*-butyl methacrylate] block-gradient copolymers

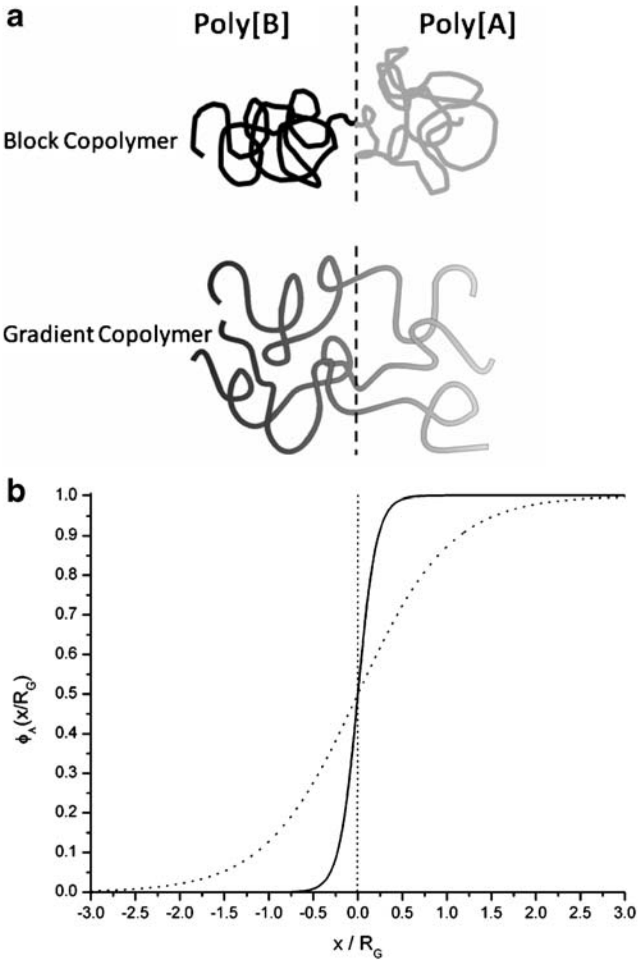

Fig. 5 **a** Schematic depiction of the molecular arrangement of a P[A]-*b*-P[B] diblock copolymer and a P[A-*grad*-B] gradient copolymer ($g(X)=-1$) as well as **b** the theoretical volume fraction distribution of the A segments of the copolymers (—=block, - - -=gradient copolymer) at the interface between two mutually immiscible polymers P[A] and P[B] [63]

[42]. Ethoxymethyl vinyl ether/methoxymethyl vinyl ether gradient copolymers were shown to form micelles in water with a broad temperature region separating the micellar and the non-micellar regions. Furthermore, a continuous transition between the molecular dispersed and the micellar state was observed on heating, where the micellar diameter decreased with ongoing micellization [75]. The observation was explained by a 'reel-in' of the gradient-corona chains caused by the diffuse interface between the micellar corona and the solution environment (Fig. 6) [76].

The aggregation behavior of block and gradient copolymers from methyl-2-oxazoline (MOX) and nony-2-oxazoline was investigated in water by means of fluorescence correlation spectroscopy [77]. P[MOX$_{0.87\mathrm{m}\%}$-*grad*-NOX$_{0.13\mathrm{m}\%}$]$_{46}$ exhibited a distinct critical micelle concentration of $\sim 8\cdot 10^{-6}$ mol/L, and the hydrodynamic diameter of the micelles was measured to 9.4 nm, compared to 2.4 nm of the unimer. When compared to an analogous diblock copolymer [78], the gradient copolymers exhibited smaller hydrodynamic radii for micelles and unimers, but a comparable CMC (P[MOX]$_{40}$-*b*-P[NOX]$_7$; $d_{\mathrm{H,Unimer}}=2.8$ nm, $d_{\mathrm{H,Micelle}}=26$ nm, CMC$=7.4\cdot 10^{-6}$ mol/L). The micellar hydrodynamic diameter of the two polymer types were both found to be of constant value over two orders of magnitude in concentration (10^{-5}–10^{-3}) mol/L. The authors did not assume distinct core–shell morphologies for the investigated gradient copolymer micelles [77].

The solution and structure formation behavior of block and gradient copolymers made from MOX and 2-phenyl-2-oxazoline (POX) were compared in ethanol/water mixtures [79]. While the gradient copolymer P[MOX$_{50\mathrm{m}\%}$-*grad*-POX$_{50\mathrm{m}\%}$] [80] was insoluble in pure water, the block copolymer PMOX$_{50}$-*b*-PPOX$_{50}$ formed worm-like micelles of 24 nm diameter. Upon addition of 5% ethanol, both the polymers dissolved under formation of coexisting cylinder and spherical micelles, but the cylinder micelles vanished above ethanol concentrations of about 15%. The micellar sizes as obtained by TEM decreased with growing alcohol content in any case; however, the block copolymer formed larger spherical micelles at any solvent composition (10% ethanol=21 nm block, 19 nm gradient; 40% ethanol=18 nm block, 11 nm gradient).

Presently, the number of published investigations is to too small to give a consistent general picture of structure formation in solution. In connection to supramolecular aspects of colloid science—as previously reviewed [81]—it may be an interesting question if complex coacervate micelles, Janus micelles, or metastable 'crew cut' micelles can also be formed by gradient copolymers. In particular, the elucidation

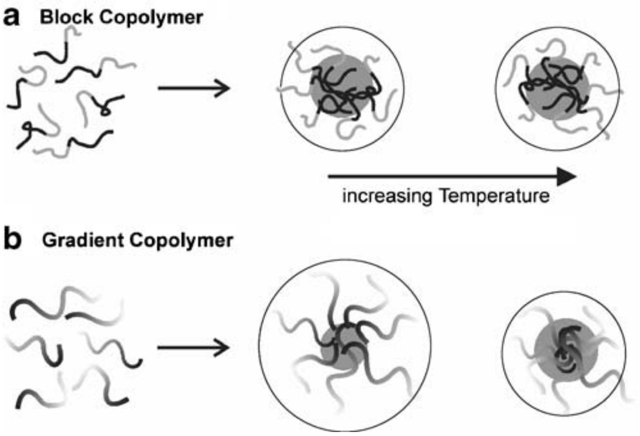

Fig. 6 Micelle formation of methoxy vinyl ether/ethoxy vinyl ether block copolymers (**a**) and gradient copolymers (**b**). While the diameters of block copolymer micelles are virtually independent of temperature, gradient copolymer micelles tend to shrink with simultaneous expansion of the core region ("reel-in effect") [76]

of differences to the well-established block copolymer systems may become a beautiful scientific game.

Applications of gradient copolymers

Because of their similarity to block copolymers, gradient polymers have been considered as a cheap alternative in applications like compatibilization of immiscible polymer blends, stabilization of emulsions or dispersions, as well as for use as thermoplastic elastomers. This may become true as soon as controlled radical polymerization can compete with anionic polymerization as a large-scale industrial technique.

Because of their peculiar ability to form broadened interphase regions, gradient copolymer are hoped to be the superior class of materials in certain fields. It has in fact been shown that styrene/methyl methacrylate gradient copolymers can act as stabilizers in polystyrene/PMMA and in polyvinyl chloride–SBS blends [82]. The addition of styrene/*n*-butyl methacrylate to molten mixtures of the respective homopolymer was demonstrated to result in blend formation and reduced phase coarsening upon annealing [83]. Polystyrene/polycaprolactone blends have successfully been prepared upon addition of styrene/4-hydroxystyrene gradient copolymers, where the compatibility between the polylactone and the gradient copolymer was made by hydrogen bonds [84]. However, up until now, the special advantages of gradient copolymers over conventional compatibilizer systems have not been demonstrated.

The extremely broad glass transition temperature ranges of gradient copolymers should make them excellent shock-absorbing or vibration-damping materials, because energy dissipation reaches a maximum value within this temperature region. In particular, a lamellar phase material with weak phase segregation that is almost entirely composed of a blurred A/B-mixed inter-phase should exhibit strong damping over a wide frequency and temperature range [86]. The structure–relaxation rate relation implied in [86] was demonstrated by dynamic mechanical analysis with the examples of styrene/4-hydroxystyrene and with styrene/*n*-butylmethacrylate constant gradient copolymers ($|g(X)| < 0.5$) [87]. Gradient polyurethane–polyisocyanurates polymers filled with barium sulfate and quartz microfibers [88] as well as cationically prepared styrene/isobutylene gradient copolymers have been discussed to serve for the same application [89]. In any case, the authors carefully avoided to compare their measurements to that of well-known vibration-damping materials.

As other possible applications for gradient copolymers adhesives (in particular pressure sensitive adhesives) [90, 91], coatings [92], dispersion [93], or wetting agents [94] have been mentioned. In any case, however, these studies have not yet revealed sufficient data to allow for a general judgment on the performance or suitability of gradient polymers as a materials class.

Summary

The synthetic techniques and strategies to prepare gradient copolymers with well-defined gradients have successfully been identified and developed during the last years. Gradient copolymers can be prepared with ‘low budget’ equipment on the laboratory scale, allowing for rapid generation of a large variety of samples with subsequent testing the suitability of the new materials for a given application. Also, feedback-loop-controlled preparation systems have been tested that may allow for large-scale, even for industrial synthesis. At the same time, theoretical considerations have revealed the main physical features of gradient copolymers, identifying possible fields of applications.

In the next future, polymer scientists come to the fascinating task of identifying the ‘right’ monomer combinations, choosing the correct gradient type, and converting their ideas into materials. Now that sound foundations of gradient copolymer science have been laid, it seems that the new polymers have to prove their value for practical (‘real world’) applications.

References

1. IUPAC (1974) Pure Appl Chem 40:477–491
2. Greszta D, Matyjaszewski K (1996) Polym Prepr 37(1):569–570
3. Arehart SV, Greszta D, Matyjaszewski K (1997) Polym Prepr 38 (1):705–706
4. Klumperman B (2007) In: Matyjaszewski K, Gnanou Y, Leibler L (eds). Macromolecular Engineering, vol. 2. Wiley, p 813–838
5. Kryszewski M (1998) Polym Adv Technol 9:244–259
6. Matyjaszewski K, Ziegler MJ, Arehart SV, Greszta D, Pakula T (2000) J Phys Org Chem 13:775–786
7. Akovali G, Biliyar K, Shen M (1975) Gov Rep Announce Index (U. S.) 75:52–77
8. Shen M, Bever MB (1972) J Mat Sci 7:741–746
9. Marchuk GI (1982) Methods of numerical mathematics, 2nd edn. Springer, New York
10. Ray WH, Gall CE (1969) Macromolecules 2:425–428
11. Odian G (1991) Principles of polymerization, 3rd edn. Wiley, New York, pp 454–457
12. Odian G (1991) Principles of polymerization, 3rd edn. Wiley, New York, p 274
13. Darling TR, Davis TP, Fryd M, Gridnev AA, Haddleton DM, Ittel SD, Matheson RR Jr, Moad G, Rizzardo E (2000) J Polym Sci A Polym Chem 38:1705–1709
14. Jouenne S, Gonzalez-Leon JA, Ruzette A-V, Lodefier P, Tence-Girault S, Leibler L (2007) Macromolecules 40:2432–2442
15. Cypryk M, Delczyk B (2006) Polimery 51:499–506
16. Chojnowski J, Cypryk M, Fortuniak W, Kazmierski K, Rozga-Wijas K, Scibiorek M (2003) ACS Symp Ser 854:12–24
17. Szwarc M (1968) Carbanions, living polymers and electron transfer process. Interscience, New York

18. Aoshima S, Kanaoka S (2008) Adv Polym Sci 210:169–208
19. Aoshima S, Sugihara S, Shibayama M, Kanaoka S (2004) Macromol Symp 215:151–163
20. Kemp LK, Storey RF (2006) Polym Prepr 47(1):149–150
21. Chojnowski J, Cypryk M, Fortuniak W, Kazmierski K, Rozga-Wijas K, Scibiorek M (2003) ACS Symp Ser 854:12–25
22. Dettmer CM, Gray MK, Torkelson JM, Nguyen SBT (2004) Macromolecules 37:5504–5512
23. Bello A, Delgado JA (2000) Rev Plast Modern 79:55–63
24. Mignard E, Leblanc T, Bertin D, Guerret O, Reed WF (2004) Macromolecules 37:966–975
25. Kim J, Torkelson JM (2007) Polym Prepr 48(1):944–945
26. Kim J, Mok MM, Sandoval RW, Woo DJ, Torkelson JM (2006) Macromolecules 39:6152–6160
27. Kim J, Zhou H, Nguyen ST, Torkelson JM (2006) Polymer 47:5799–5809
28. Karaky K, Billon L, Pouchan C, Desbrières J (2007) Macromolecules 40:458–464
29. Cuervo-Rodrigues R, Bordege V, Fernandez-Monreal MC, Fernandez-Garcia M, Madruga EL (2004) J Polym Sci A 42:4168–4176
30. Karaky K, Père E, Pouchan C, Garay H, Khoukh A, Francois J, Desbrierees J, Billon L (2006) New J Chem 30:698–705
31. Karaky K, Clisson G, Reiter G, Billon L (2008) Macromol Chem Phys 209:715–722
32. Gray MK, Zhou H, Nguyen SBT, Torkelson JM (2004) Macromolecules 37:5586–5595
33. Moad G, Rizzardo E, Thang SH (2008) Polymer 49:1079–1131
34. Rizzardo E, Chiefari J, Chong BYK, Ercole F, Krstina J, Jeffery J, Le TPT, Mayadunne RTA, Meijs GF, Moad CL, Moad G, Thang SH (1999) Macromol Symp 143:291–307
35. Goebelt B (2007) EU Patent, EP 1803753 A2 (to: BYK-Chemie GmbH, Germany), 07.04. (CA 147:144928).
36. Lutz J-F, Pakula T, Matyjaszewski K (2003) ACS Symp Ser 854:268–282
37. Matyjaszewski K, Xia J (2001) Chem Rev 101:2921–2990
38. Matyjaszewski K, Ziegler MJ, Arehart SV, Greszta D, Pakula T (2000) J Phys Org Chem 13:775–786
39. Fu Y, Cunningham MF, Hutchinson RA (2007) Macromol Symp 259:151–163
40. Kim J, Torkelson JM (2007) Polym Prepr 48(1):221–222
41. Qin S, Saget J, Pyun J, Jia S, Kowalewski T, Matyjaszewski K (2003) Macromolecules 36:8969–8977
42. Lee SB, Russell AJ, Matyjaszewski K (2003) Biomacromolecules 4:1386–1393
43. Qin S, Pyun J, Saget J, Jia S, Kowalewski T, Matyjaszewski K (2002) Polym Prepr 43(2):235–236
44. Börner HG, Duran D, Matyjaszewski K, da Silva M, Sheiko SS (2002) Macromolecules 35:3387–3394
45. Shinoda H, Miller PJ, Matyaszewski K (2001) Macromolecules 34:3186–3194
46. Greszta D, Matyjaszewski K (1997) Polym Prepr 38(1):707–708
47. Skeist I (1946) J Amer Chem Soc 68:1781–1784
48. Gu B, Sen A (2002) Macromolecules 35:8913–8916
49. Fujisawa T, Penlidis A (2008) J Macromol Sci 45:115–132
50. Beginn U (2006) Polymer 47:6880–6894
51. Kotani Y, Kamigaito M, Sawamoto M (1998) Macromolecules 31:5582–5587
52. Greszta D, Matyjaszewski K, Pakula T (1997) Polym Prepr 38 (1):709–710
53. Dube MA, Soares JBP, Penlidis A, Hamielec AE (1997) Ind Eng Chem Res 36:966–1015
54. Hamielec AE, MacGregor JF, Penlidis A (1987) Makromol Chem Macromol Symp 10/11:521–570
55. Wang R, Luo Y, Li BG, Sun X, Zhu S (2006) Macromol Theory Simul 15:356–368
56. Wang R, Luo Y, Li BG, Zhu S (2007) AIChE 53:174–186
57. Sun X, Luo Y, Wang R, Li BG, Zhu S (2007) Macromolecules 40:849–859
58. Schmitz C, Beginn U, Möller M (2008) Polymer submitted.
59. Pakula T (1996) Macromol Theory Simul 5(5):987–1006
60. Aksimentiev A, Hoyst R (1999a) Prog Polym Sci 24:1045–1093
61. Aksimentiev A, Hoyst R (1999b) J Chem Phys 111:2329–2339
62. Jiang R, Jin Q, Li B, Ding D, Wickham RA, Shi A-C (2008) Macromolecules 41:5457–5465
63. Shull KR (2002) Macromolecules 35:8631–8639
64. Lefebvre MD, Olvera de la Cruz M, Shull KR (2004) Macromolecules 37:1118–1123
65. Matyjaszewski K, Ziegler MJ, Arehart SV, Greszta D, Pakula T (2000) J Phys Org Chem 13:775–778
66. Karaky K, Pere E, Pouchan C, Desbrieres J, Derail C, Billon L (2006) Soft Mat 2:770–778
67. Shinoda H, Matyjaszewski K, Okrasa L, Mierzwa M, Pakula T (2003) Macromolecules 36:4772–4778
68. Lee H-il, Matyjaszewski K, Yu S, Sheiko SS (2005) Macromolecules 38:8264–8271
69. Mok MM, Pujari S, Burghardt WR, Dettmer CM, Nguyen SBT, Ellison CJ, Torkelson JM (2008) Macromolecules 41:5818–5829
70. Pickett GT (2003) J Chem Phys 118:3898–3903
71. Lefebvre MD, Dettmer CM, McSwain RL, Xu C, Davila JR, Composto RJ, Nguyen SBT, Shull KR (2005) Macromolecules 38:10494–10502
72. Gohy J-F (2005) Advances in Polymer Science 190(Block Copolymers II):65–136
73. Hamley IW (2005) Block copolymers in solution—fundamentals and application, chap. 2. Wiley, Chichester
74. Wong CLH, Kim J, Roth CB, Torkelson JM (2007) Macromolecules 40:5631–5633
75. Okabe S, Fuse C, Sugihara S, Aoshima S, Shibayama M (2006) Physica B: Cond Matter 385–386:756–758
76. Okabe S, Seno K, Kanaoka S, Aoshima S, Shibayama M (2006) Macromolecules 39(4):1592–1597
77. Bonne TB, Lüdtke K, Jordan R, Papadakis CM (2007) Macromol Chem Phys 208:1402–1408
78. Bonne TB, Lüdtke K, Jordan R, Papadakis CM (2007) Coll Polym Sci 5:491–497
79. Hoogenboom R, Thijs HML, Wouters D, Hoeppener S, Schubert US (2008) Macromolecules 41:1581–1583
80. Hoogenboom R, Thijs HML, Fijten MWM, Van Lankvelt BM, Schubert US (2007) J Polym Sci, Part A: Polym Chem 45:416–422
81. Stuart CMH (2008) Coll Polym Sci 286:855–864
82. Wang T, Liu F, Luo N, Ying S, Liu Q (2001) Hech Xiang Gon 24:328–330
83. Kim J, Gray MKJ, Zhi H, Nguyen SBT, Torkelson JM (2005) Macromolecules 38:1037–1040
84. Tao Y, Kim J, Torkelson JM (2006) Polymer 47:6773–6781
85. Kim J, Zhou H, Nguyen SBT, Torkelson JM (2006) Polymer 47:5799–5809
86. Hashimoto T, Tsukahara Y, Tachi K, Kawai H (1983) Macromolecules 16:648–657
87. Mok M, Kim J, Torkelson JM (2008) J Polym Sci B Polym Phys 46:48–58
88. Askadskii AA, Luchkina LV, Nikiforova GG, Kovriga OV (2007) Plasti Mass 30–33
89. Kemp LK, Storey RF (2006) Abstracts 231st ACS Nation. Meet., March 26–30, 2006
90. Kano Y (2002) Hikaku Kagaku (Science) 48:109–121
91. Genzer J, Bhat R, Tomlinson M (2004) Proc Ann Meet Adhes Soc 27:47–48
92. Goebelt B (2004) FATIPEC Congress 27th(1):303–312
93. Hu Z, Tao M, Zhang Z (2007) Coll Surf A 302:307–311
94. Goebelt B, Omeis J, Johann S, Koehler S (2008) PCT Int Appl WO. 2008043529 A2 20080417 (to: Byk-Chemie GmbH, Germany)