JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2000; **13:** 775–786

Gradient copolymers by atom transfer radical copolymerization

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Received 15 May 2000; revised 28 July 2000; accepted 29 July 2000

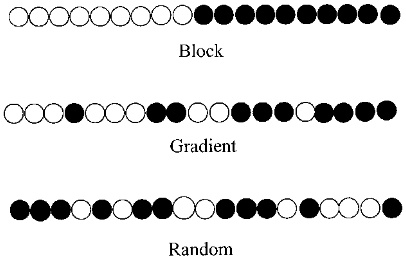
ABSTRACT: Gradient copolymers, in which the instantaneous composition varies continuously along each chain, are discussed in terms of theoretical background, significance and examples from the literature. The specific focus is the use of atom transfer radical polymerization to synthesize gradient copolymers with various composition profiles. Examples of gradient copolymers using ionic and controlled radical polymerization techniques are presented. Atom transfer radical polymerization has been used under both batch and semi-batch conditions to produce gradient copolymers. The physical properties of gradient copolymers and possible future work in the field of gradient copolymers are discussed. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: gradient copolymers; atom transfer radical polymerization

INTRODUCTION

It is the purpose of this paper to discuss an interesting class of materials, gradient copolymers, and in particular to report the use of atom transfer radical polymerization (ATRP) to prepare them. The constantly advancing technologies of the world demand newer, higher performance and more specialized materials to make this technical progress become a reality. One solution to this problem, which has recently been receiving attention, is the preparation and use of gradient materials.[1,2] These gradient materials blend the properties of two or more materials in a continuous manner from one area of the material to another. Two methods of making gradient materials have been studied.[2] The first is the construction of macroscopic gradient materials, in which several homopolymers are prepared sequentially on a surface of other material. The various homopolymers and copolymers diffuse within the gradient material leading to a continuous and systematic macroscopic change in the composition of the material. In this way the polymers synthesized are chemically homogeneous, but the bulk material is heterogeneous in composition. Materials of this type have been reported from several sources, and they have demonstrated numerous interesting properties,[2,3] leading to their use in such applications as high-bandwidth optical fibers.[3]

The second method of producing gradient materials relies on the gradient copolymers or molecular gradients and will be the primary focus of this report. Gradient copolymers are copolymers in which the instantaneous composition varies continuously along the chain contour.[1,4] This is in contrast to block copolymers, in which the instantaneous composition changes discontinuously along the chain. As shown in Scheme 1, composition along the chain varies in different ways for block, gradient and random copolymers. The composition does not vary in a block copolymer until after the crossover point between blocks, a random copolymer shows no continuous change in composition and gradient copolymers have a continuous change in composition from one end of the chain to the other. In order to achieve this



Scheme 1. Schematic representation of the composition in block, gradient and statistical copolymers, in which the open circles denote monomer 1 and the closed circles monomer 2

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Contract/grant sponsor: NSF.
Contract/grant sponsor: EPA.
Contract/grant sponsor: ATRP Consortium.

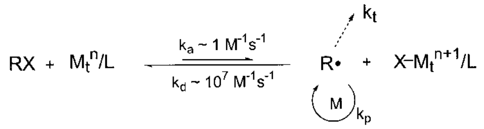
continuous change in instantaneous composition, all chains must be initiated simultaneously, and must survive until the end of the polymerization. Therefore, a living (ionic) or controlled/living radical polymerization technique must be employed, as the significant presence of chain-breaking reactions would lead to heterogeneity in both composition and molecular weight.

In addition to these mechanistic requirements, synthesizing well-defined gradient copolymers also requires facile cross-propagation. This is very hard to fulfill in ionic copolymerizations since reactivities for monomers in ionic systems do not favor cross-propagation.[5] In contrast, free radical polymerization abounds with examples of monomers that easily cross-propagate.[6] Therefore, for synthesizing a well-defined gradient copolymer, controlled free radical copolymerizations offer a very attractive and powerful option. As the use of ATRP to form these gradient copolymers is the focus of this paper, it is necessary to provide a discussion of the fundamentals of ATRP and controlled radical polymerizations in general.

Controlled radical polymerization

The field of controlled radical polymerization (CRP) has become the subject of intense interest and research, despite the relatively recent birth of the field.[7–13] CRP systems are polymerizations in which the significance of chain-breaking reactions is suppressed to essentially negligible levels. This suppression is typically achieved by means of a dynamic exchange between minute amounts of active propagating radicals and the predominant dormant species.[7] These dormant species do not possess an active radical site and cannot propagate or participate in transfer or bimolecular termination reactions. The suppression of chain-breaking reactions in CRP leads to the uniform growth of chains, resulting in polymers with well-defined molecular weights, narrow molecular weight distributions and a high level of end-group functionality.[7]

One particular type of CRP that has been shown to be robust, versatile and convenient is ATRP.[9–11,14] As shown in Scheme 2, the ATRP process begins with the activation of an alkyl halide (or pseudo-halide), RX, by the reversible abstraction of the halogen by a transition metal complex, M_t^n/L, to form the active radical species, $R^{\cdot}$, which initiates polymerization. Since the halogen abstraction is reversible, a dynamic equilibrium is established between the active, propagating radical species and the dormant halogen-capped species. Since, in this equilibrium, the rate of deactivation, k_d, is very large compared with the rate of activation, k_a, the chains are predominantly in the dormant state. The active radical species propagate, k_p, and terminate, k_t, as in a conventional radical polymerization. However, the proportion of chains which have been terminated is much smaller than that of the dormant species. Thus, the system strongly resembles a living polymerization.



Scheme 2. Schematic representation of the ATRP process. M_t represents a transition metal, L represents the ligands complexed to the transition metal and RX is an alkyl (pseudo)halide

Both the high level of end-group functionality and the lifetime of the polymer chains in CRP (and in ATRP in particular) make this method attractive for synthesizing gradient copolymers. As discussed above, end groups are conserved in these reactions since chain-breaking reactions are significantly suppressed. In addition, the existence of the dynamic exchange, which strongly favors the dormant species greatly increases the lifetime of a polymer chain.[15] In a conventional radical polymerization a polymer chain is initiated, propagates to its maximum degree of polymerization and terminates, all within a matter of seconds.[6] However, in a CRP the time between the initiation of a chain and the end of propagation is of the order of hours.[9,10,15] These differences between conventional and controlled radical polymerizations allow for a greater opportunity for chain modifications and lead to the great extent of control that CRP gives over topology,[12,16–19] sequential composition[20–23] and instantaneous composition of a polymer chain.[4,24–28]

Since the active species in these polymerizations are radicals, CRPs have many of the same advantages of conventional radical copolymerizations, including a high level of tolerance to moisture and other impurities.[9,10] However, the similarity that will be of most concern to gradient copolymers is the similarity of the chemoselectivities of the two types of polymerization. Since in both methods propagation occurs through a free radical mechanism, monomer pairs should have similar reactivity ratios in a CRP and a conventional radical polymerization, as observed by several laboratories.[25,29–32] Some small discrepancies are expected, and have been observed, in the values of reactivity ratios from ATRP and conventional radical polymerizations.[33] There are a number of reasons for these discrepancies, such as obvious differences in reaction temperatures and solvent. Additionally, differences in the rate of chain growth can also alter the observed reactivity ratios, in that in a controlled polymerization polymer is slowly formed throughout the reaction, whereas in a conventional system high polymer is formed at the beginning of the reaction and the composition of the polymer is established at low conversion. This difference may also amplify the so-called 'bootstrap' effect proposed by Harwood.[34] The presence of a transition metal catalyst in these polymerizations further complicates the picture by introducing the possibility of complexation of some monomers with the weakly Lewis acidic transition metal catalysts.[35] The final, and perhaps most important, cause of discrepancies in reactivity ratios observed in ATRP is the differences in methodologies of measuring reactivity ratios in controlled and conventional radical polymerizations. In a conventional process the monomer reactivity ratios can be measured at low conversion with different monomer feeds. However, in the ATRP process high polymer is not formed immediately in the reaction. Measurements at low conversions could be affected by the structure of the initiator, which may react preferentially with one comonomer. For this reason, it is necessary to measure the cumulative composition of the copolymers at a conversion higher than would be studied in a conventional process. However, as the cumulative composition of a copolymer will always be equal to the monomer feed at 100% monomer conversion, the closer the reaction gets to 100% conversion, the less precise information on reactivity ratios can be obtained. Thus, the conversion range 20% to 50% may be most appropriate.

It has been shown previously, however, that the reactivity ratios of a monomer pair are not affected by differences in the relative activation and deactivation rates of the monomers.[29,31,33] Another report from this laboratory shows that several unique behaviors seen in copolymerizations using ATRP are caused by significant differences in the values of the activation/deactivation equilibrium constants of the two monomers, but the reactivity ratios remain unaffected.[29]

Gradient copolymers

In a batch copolymerization using a controlled/living polymerization technique such as ATRP, a gradient is produced spontaneously due to the feed composition drift that occurs during the reaction. In a non-living system this drift is manifested in a change in composition among the chains, whereas in living polymerization the change in composition occurs in each chain. We will apply here a terminal model, meaning that we ignore the effect of penultimate units and consider only two homopropagation and two cross-propagation steps; the ratio of the corresponding rate constants defines the reactivity ratio for monomer 1 (r_1) and monomer 2 (r_2). In systems which obey the terminal model, the compositional drift can be explained by considering the equation

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{1}$$

where r_1 and r_2 are the reactivity ratios, f_1 and f_2 are the mole fractions of monomers 1 and 2 in the monomer feed and F_1 is the mole fraction of units from monomer 1 in the copolymer.[36]

Under equimolar feed conditions f_1 (and f_2) will change due to preferential polymerization of one of the monomers (unless $r_1 = r_2$), resulting in a continuous change in F_1 (copolymer composition). This continuous change of F_1 results in a composition gradient, the significance of which depends on the reactivity ratios of the two monomers being polymerized and their concentration in the initial reaction feed.

Cumulative and instantaneous compositions are calculated from Eqns (2) and (3), [27] respectively

$$F_{cum,1} = \frac{(\%\text{conv})_1 [M_1]_0}{(\%\text{conv})_1 [M_1]_0 + (\%\text{conv})_2 [M_2]_0} \tag{2}$$

$$F_{inst,1} = F_{cum,1} + (\%\text{conv}) \frac{\Delta F_{\text{cum},1}}{\Delta(\%\text{conv})} \tag{3}$$

where (% conv)$_1$ denotes the conversion of monomer 1 and [M$_1$]$_0$ denotes the initial concentration of monomer (subscripts 1 denote monomer 1). In general, plotting composition versus chain length helps to visualize the composition changes occurring over the length of the chain. The *x*-axis, in plots of composition versus chain length, can also be conversion, since the two are related by the equation

$$\overline{X}_n = \frac{\Delta[M]}{[I]_0} \tag{4}$$

Figures 1 and 2 plot the cumulative and instantaneous copolymer composition versus chain length for simulated statistical copolymerizations of two monomers whose

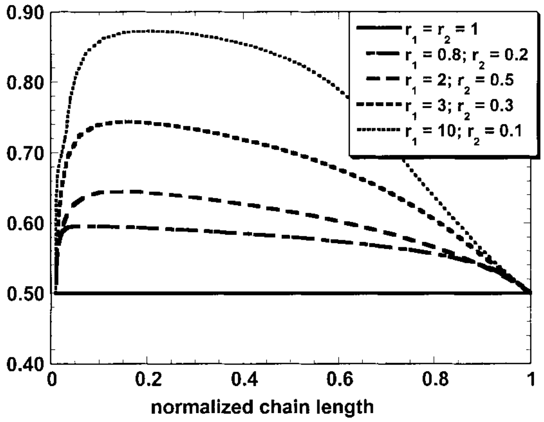


Figure 1. Simulated F_{cum}, M$_1$ versus normalized chain length for a living batch copolymerization of M$_1$ and M$_2$ with different reactivity ratios. [M$_1$]$_0$ = [M$_2$]$_0$ = 5 M; [I]$_0$ = 0.1 M. Rate constants of initiation for both monomers are assumed to be equal

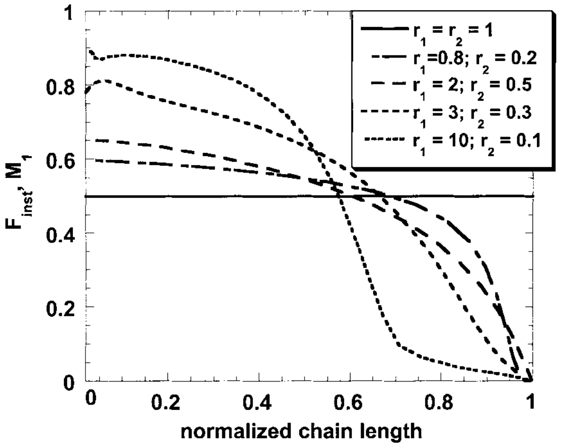


Figure 2. Simulated F_{inst}, M_1 versus normalized chain length for a living batch copolymerization of M_1 and M_2 with different reactivity ratios. $[M_1]_0 = [M_2]_0 = 5$ M; $[I]_0 = 0.1$ M. Rate constants of initiation for both monomers are assumed to be equal

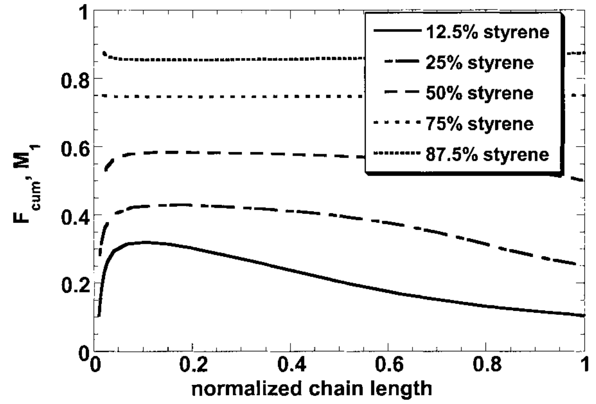


Figure 3. F_{cum}, M_1 for a simulated living batch copolymerization with reactivity ratios $r_1 = 0.8$ and $r_2 = 0.2$ with different monomer feed ratios. $[M]_0 = 10$ M; $[I]_0 = 0.1$ M. Rate constants of initiation for both monomers are assumed to be equal

concentrations in the feed are equal. These figures resemble the dependence of cumulative composition on conversion in a conventional radical polymerization. In a living system, however, this composition change will be evident along the chain, whereas in a conventional radical polymerization this change in composition would be manifested among chains made at different times during the reaction.

From Fig. 2, it is seen that the gradient is non-existent for monomer pairs with reactivity ratios which are $r_1 = r_2$. Figure 2 also illustrates that for pairs with both reactivity ratios <1, in this case $r_1 = 0.8$ and $r_2 = 0.2$ (to model the behavior of styrene and *n*-butyl acrylate),[25] the change in instantaneous composition is relatively small. The gradient is seen to be much stronger for copolymerizations with large differences in the values of the two reactivity ratios. Three examples of this behavior are shown in Fig. 2, $r_1 = 2$; $r_2 = 0.5$ (approximate model of methyl methacrylate and methyl acrylate),[37] $r_1 = 3$; $r_2 = 0.3$ (model of methyl methacrylate and *n*-butyl acrylate),[29] and $r_1 = 10$; $r_2 = 0.1$ (model of methyl methacrylate and vinyl chloride).[38] As the differences in the two values of reactivity ratio increase, so does the steepness of the gradient in instantaneous composition.

Figures 3 and 4 show cumulative and instantaneous composition in a copolymerization of styrene with *n*-butyl acrylate with constant reactivity ratios ($r_1 = 0.8$; $r_2 = 0.2$) but different initial monomer feed ratios. The variance in the gradient is much more visible in the plot of instantaneous composition (Fig. 4) than in the plot of cumulative composition (Fig. 3). Figure 4 demonstrates that changing the initial monomer feed of the two monomers significantly affects the shape of the gradient. There is essentially no variation in instantaneous composition at $f_1 = 0.75$ in the feed, owing to the nearly azeotropic conditions of this reaction (azeotropic copolymerization would occur at $f_1 = 0.80$ in this system). As the shape of the gradient formed in batch copolymerizations depends on the reactivity ratios of the two monomers being polymerized and their relative concentrations, additional manipulation of the shape of the gradient may be accomplished by feeding one comonomer during the polymerization, i.e. in a semi-batch process.

EXAMPLES OF GRADIENT COPOLYMERS

Gradient copolymers from living ionic polymerization

The first living polymerizations employed anionic mechanisms.[5] Since controlled/living polymerizations are

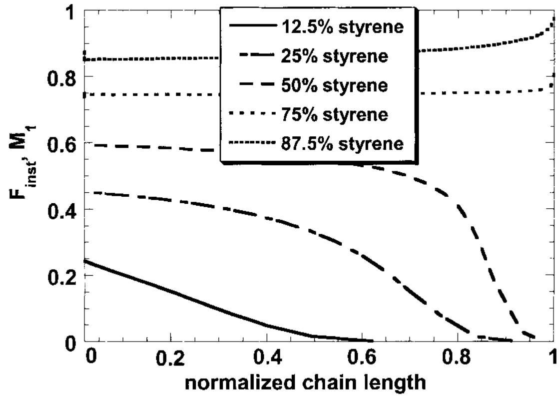


Figure 4. F_{inst}, M_1 for a simulated living batch copolymerization with reactivity ratios $r_1 = 0.8$ and $r_2 = 0.2$ with different monomer feed ratios. $[M]_0 = 10$ M; $[I]_0 = 0.1$ M. Rate constants of initiation for both monomers are assumed to be equal

required for the synthesis of gradient copolymers, it follows that the first reported examples of gradient copolymers were based on living anionic polymerizations.[39–43] The most common examples of gradient copolymers prepared anionically are copolymers of styrene, or styrene derivatives, with butadiene or isoprene[40–43] and copolymers of ethylene oxide and butylene oxide.[44] These copolymers have been prepared by both simultaneous copolymerization of the two monomers[42–44] and by the partial homopolymerization of one monomer followed by the introduction of the second monomer which was then copolymerized with the first monomer resulting in a 'tapered block' architecture.[40,41] Living anionic polymerizations have some drawbacks such as the rigorous purification required for these polymerizations and large differences in the reactivity ratios of anionic monomers, which limits the monomer pairs that can be employed.[5] Recently introduced CRP techniques offer a convenient alternative to living ionic polymerizations.

Gradient copolymers from controlled radical polymerizations

The use of CRP techniques to synthesize gradient copolymers has not, as yet, been very thoroughly explored. The use of stable free radical (nitroxide mediated)[22,45–50] and ATRP[1,24–30,32,51,52] techniques in simultaneous copolymerization has been reported to a limited extent. The use of nitroxide mediated polymerization has been shown to be effective for the synthesis of not only homopolymers and block copolymers, but also random and statistical copolymers of styrene. Examples of copolymerization of styrene with comonomers such as 4-hydroxystyrene,[45] 4-acetoxystyrene,[45] *n*-butyl acrylate,[48] butadiene,[47] methyl methacrylate,[49] chloromethylstyrene,[50] acrylonitrile,[22] 2-hydroxyethyl methacrylate,[49] 4-(hydroxymethyl)styrene,[49] vinylpyrrolidone[49] and maleic anhydride[46] have recently been reported. These reports indicate that copolymers of these comonomers with styrene can be formed using a nitroxide-mediated CRP. The gradient nature of these copolymers has only been explored in a few of these reports, and in many cases the monomer feeds and reactivity ratios were not conducive to the formation of substantial gradients in instantaneous composition. Also, owing to the nature of nitroxide-mediated CRP, many reports showed that as the amount of styrene in the monomer feed was decreased, the level of control in the polymerization decreased, as evidenced by increased polydispersities. The introduction of new more universal nitroxide mediators[53,54] will allow for the synthesis of a wider range of gradient copolymers with acrylates and acrylamides.

Several reports have also claimed the synthesis of gradient copolymers by iniferter techniques.[55–57] Copolymers in these systems displayed rather broad molecular weight distributions ($M_W/M_n > 2$), suggesting heterogeneity in both composition and molecular architecture (no precise composition data were reported).

One of the newest methods of CRP is reversible addition–fragmentation chain transfer (the RAFT process).[13] Although no examples of simultaneous copolymerization using RAFT have yet been reported, the RAFT process should be just as useful for the synthesis of gradient copolymers as any of the other CRP techniques. The use of ATRP to prepare gradient copolymers will be discussed in detail below.

Examples from ATRP

A number of authors have reported the use of ATRP for the synthesis of statistical copolymers, and several of these reports have targeted the study of the gradient nature of these copolymers.[24–26,28–30,32,51,52] Two methods of gradient copolymer synthesis have been reported. The first is the use of batch copolymerizations in which a spontaneous gradient in instantaneous composition is formed based on the differences in the reactivity ratios of the comonomers, and the concentrations of comonomers in the monomer feed.[24–26,28–30,51,52] The second method is the use of semi-batch copolymerizations to form controlled gradients in instantaneous composition.[24,26,32]

Batch copolymerization

Batch copolymerization using ATRP to prepare gradient copolymers has been shown to be successful for a number of monomer pairs. Work performed in this laboratory using batch copolymerization has, thus far, focused on styrene–acrylates[24,25,58] and methyl methacrylate–acrylates[26,29] based gradient copolymers. Figure 5 illustrates the results of several styrene–*n*-butyl acrylate copolymerizations.[25] At the three different styrene feed conditions, the measured values of cumulative composition agree well with the dependence predicted by simulations of the copolymerization, using $r_S = 0.8$ and $r_{nBA} = 0.2$. This figure shows that composition measured from NMR analysis agrees well with composition calculated from conversion data measured using gas chromatography. Some small deviations in cumulative composition are observed in Fig. 5. These deviations would be greatly amplified in the calculation of instantaneous composition, making these calculations, in some cases, limited in significance.

The composition gradient observed for the batch copolymerization of styrene and *n*-butyl acrylate is not very large, and demonstrates some limitations of batch copolymerization processes. In a batch process, the reactivity ratios of the monomer pair strongly limits the shape and significance of the composition gradient that

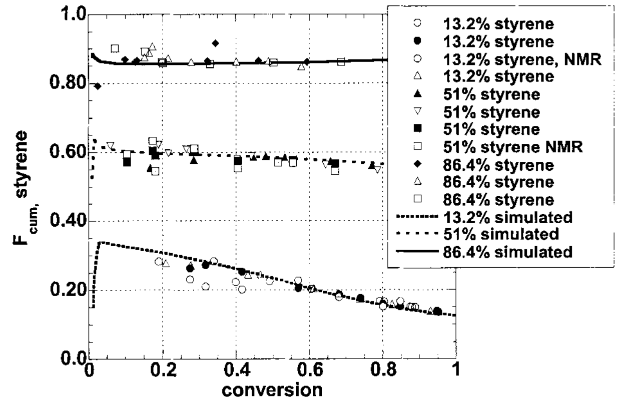


Figure 5. F_{cum}, styrene for the simultaneous copolymerizations of styrene and *n*-butyl acrylate, initiated with methyl 2-bromopropionate and catalyzed with CuBr–2(4,4′-di(5-nonyl)-2,2′-bipyridine) at 110 °C, $[M]_0{:}[I]_0 = 100{:}1$. Simulations used $r_S = 0.8$ and $r_{nBA} = 0.2$; rate constants of initiation for both monomers are assumed to be equal. Different symbols correspond to different experiments characterized either by GC or NMR

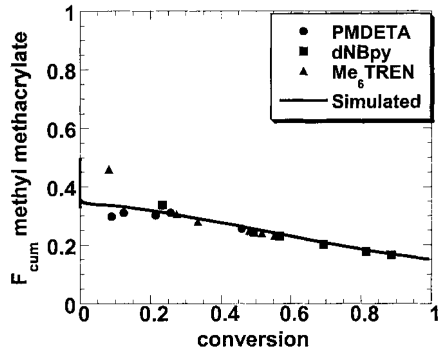


Figure 6. F_{cum}, methyl methacrylate for the simultaneous copolymerizations of methyl methacrylate and *n*-butyl acrylate, initiated with methyl 2-bromopropionate and catalyzed with CuBr–2(4,4′-di(5-nonyl)-2,2′-bipyridine) (dNbpy) in bulk at 90 °C ($[M]_0{:}[I]_0{:}[\text{catalyst}] = 300{:}1{:}1$), CuBr–N,N,N′,N′,N″-pentamethyldiethylenetrimamine (PMDETA) in bulk at 60 °C ($[M]_0{:}[I]_0{:}[\text{catalyst}] = 300{:}1{:}1$), and CuBr–tris[2-(dimethylamino)ethyl]amine (Me_6TREN) in 20% (v/v) ethylene carbonate at 60 °C ($[M]_0{:}[I]_0{:}[Cu(I)Br]_0{:}[Cu(II)Br]_0{:}[\text{ligand}]_0 = 300{:}1{:}0.5{:}0.1{:}0.6$). In all cases the initial monomer feed contained 15% methyl methacrylate. Simulations used $r_{MMA} = 3.0$ and $r_{nBA} = 0.3$; rate constants of initiation for both monomers are assumed to be equal

can be formed. This is also shown in recent work by Sawamoto and co-workers[32] using a batch copolymerization of styrene–methyl methacrylate, and by Li and co-workers,[51] using a batch copolymerization of styrene and various maleimides. Owing to the similar reactivity ratios of styrene and methyl methacrylate ($r_{\mathrm{Styrene}} \approx r_{\mathrm{MMA}} \approx 0.5$), the polymers prepared in a batch process must be essentially random (Sawamoto and co-workers ingenious method of avoiding this will be discussed below), and in the case of styrene and maleimides the reactivity ratios of monomers ($r_{\mathrm{Styrene}} \approx r_{\mathrm{Malemides}} \approx 0$) dictate that nearly alternating copolymers have been formed.

The use of ATRP in the batch copolymerization of methyl methacrylate with various (meth)acrylates has also been reported recently by a number of laboratories.[26,29,30,52] Work recently completed in this laboratory has shown that the batch copolymerization of methyl methacrylate–*n*-butyl acrylate could be used to prepare gradient copolymers using a variety of ATRP catalyst systems. Figure 6 shows the cumulative composition of methyl methacrylate in three copolymers prepared using three different catalysts at a constant initial monomer feed containing 15% methyl methacrylate.[29] This particular monomer feed condition was chosen owing to the effectiveness of all three catalyst systems studied at this monomer feed. At high concentrations of methyl methacrylate the Me_6TREN catalyst did not give controlled polymerization. This plot provides agreement between the various experimental points and the dependence predicted by simulations of the reactions using $r_{\mathrm{MMA}} = 3.0$ and $r_{\mathrm{nBA}} = 0.3$. The instantaneous composition versus conversion (chain length) is shown in Fig. 7. These two composition plots demonstrate that the batch copolymerization of methyl methacrylate and *n*-butyl acrylate results in a copolymer with a significant gradient in both instantaneous and cumulative composition. This work demonstrates that an appreciable gradient can be formed in a batch copolymerization if the reactivity ratios of the monomer pair are sufficiently different.

Sawamoto and co-workers have reported the batch copolymerization of methyl methacrylate both with *n*-

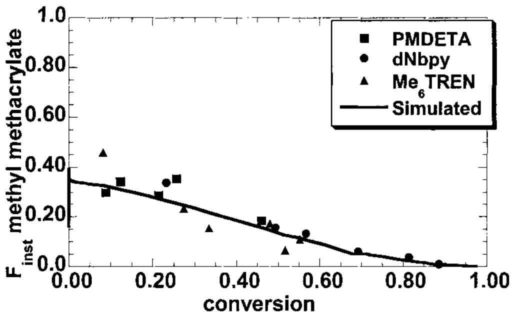


Figure 7. F_{inst}, methyl methacrylate for the simultaneous copolymerizations of methyl methacrylate and *n*-butyl acrylate, initiated with methyl 2-bromopropionate and catalyzed with CuBr–2(4,4′-di(5-nonyl)-2,2′-bipyridine) (dNbpy) in bulk at 90 °C ($[M]_0{:}[I]_0{:}[\text{catalyst}] = 300{:}1{:}1$), CuBr–N,N,N′,N′,N″-pentamethyldiethylenetrimamine (PMDETA) in bulk at 60 °C ($[M]_0{:}[I]_0{:}[\text{catalyst}] = 300{:}1{:}1$) and CuBr–tris[2-(dimethylamino)ethyl]amine (Me_6TREN) in 20% (v/v) ethylene carbonate at 60 °C ($[M]_0{:}[I]_0{:}[Cu(I)Br]_0{:}[Cu(II)Br]_0{:}[\text{ligand}]_0 = 300{:}1{:}0.5{:}0.1{:}0.6$). In all cases the initial monomer feed contained 15% methyl methacrylate. Simulations used $r_{MMA} = 3.0$ and $r_{nBA} = 0.3$; rate constants of initiation for both monomers are assumed to be equal

butyl acrylate and with methyl acrylate, using a nickel-based ATRP catalyst system.[52] It can be assumed that these copolymers were in fact gradient copolymers with fairly significant changes in composition along the polymer chain. Haddleton *et al.* reported a thorough investigation of monomer reactivity ratios in which ATRP and several other living polymerization methods were used to copolymerize methyl methacrylate and *n*-butyl methacrylate.[30] The focus of this paper was the comparison of reactivity ratios obtained from the different polymerization mechanisms. Based on the small differences in the reactivity ratios of this monomer pair, however, it must be assumed that the composition gradients in these polymerizations were not very significant.

These reports show that, under the correct conditions, gradient copolymers can be made in batch copolymerizations using ATRP. However, in a batch process, the strength of the gradient is dictated only by the reactivity ratios of the monomer pair and initial monomer feed and cannot be further controlled.

Semi-batch copolymerization

Continuously adding one comonomer to a copolymerization is a way to form a more significant compositional gradient along the chain. The formation of the gradient is influenced by continuous changes in the monomer feed caused by addition of the comonomer. Using these two concepts, one can synthesize a larger range of possible composition gradients for a given monomer pair, since effects caused by differences in reactivity ratios can be compensated through appropriate rates and order of addition of one monomer to the other. That is, strong gradients of monomers such as styrene and *n*-butyl acrylate can be formed by choosing appropriate experimental conditions, even though these monomers form small gradients in batch processes.

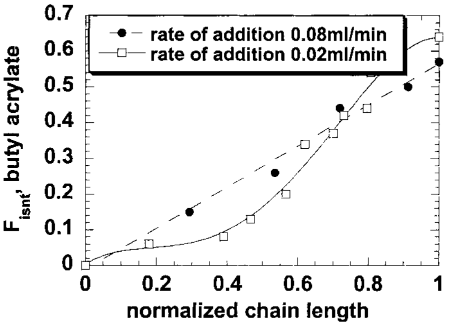


Figure 8. F_{inst}, *n*-butyl acrylate for copolymerizations of styrene and *n*-butyl acrylate, initiated with methyl 2-bromopropionate and catalyzed with CuBr–2(4,4′-di(5-nonyl)-2,2′-bipyridine) at 110 °C. $[Styrene]_0:[I]_0:[catalyst]_0 = 8.7:0.04:0.04$, with continuous addition of *n*-butyl acrylate at a rate as indicated. Initial volume of styrene, 7.7 ml

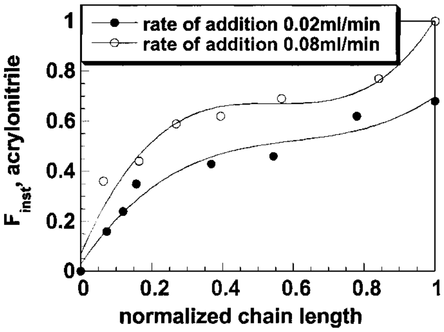


Figure 9. F_{inst}, acrylonitrile for copolymerizations of styrene and acrylonitrile, initiated with 1-phenylethyl bromide and catalyzed with CuBr–2(2,2′-bipyridine) at 80 °C. $[Styrene]_0:[I]_0:[catalyst]_0 = 8.7:0.1:0.1$, with continuous addition of acrylonitrile at a rate as indicated. Initial volume of styrene, 10.0 ml

The control of compositional gradient through the use of controlled monomer addition has been demonstrated through the atom transfer radical copolymerization of styrene and *n*-butyl acrylate. Figure 8 shows that by slowly adding *n*-butyl acrylate to a batch polymerization of styrene a much more significant gradient in composition is obtained, as opposed to the behavior of this monomer pair in a batch copolymerization, as discussed above.[24] It is also shown that the shape and significance of the composition can both be manipulated by changing the rate and order of monomer addition. The lines connecting the data points in Fig. 8 and the following composition plots are meant only as guides to the eye.

Semi-batch copolymerization can allow the formation of a gradient copolymer when the two monomers tend to polymerize in an alternating fashion, as is the case in the copolymerization of styrene and acrylonitrile. Figure 9 shows the instantaneous composition versus chain length for two rates of addition, demonstrating that adding monomer to the copolymerization mixture results in an instantaneous composition different from what would be

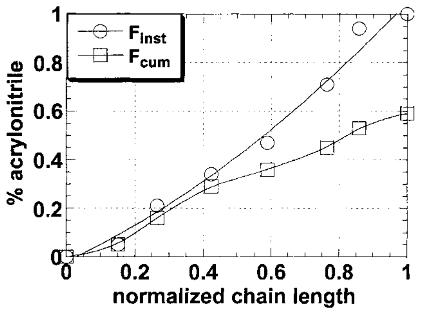


Figure 10. F_{inst}, acrylonitrile and F_{cum}, acrylonitrile for the copolymerization of styrene and acrylonitrile, initiated with 1-phenylethyl bromide and catalyzed with CuBr–2(2,2′-bipyridine) at 80 °C. $[Styrene]_0:[I]_0:[catalyst]_0 = 8.7:0.1:0.1$, with continuous addition of acrylonitrile at a rate of 0.01 ml min^{-1}. Initial volume of styrene, 10.0 ml

expected for two monomers with alternating tendencies.[28] Furthermore, the rate of addition influences the gradient formed in these two reactions, as was observed in the case of *n*-butyl acrylate and styrene. Both the cumulative and instantaneous composition of copolymer prepared through the semi-batch copolymerization of styrene and acrylonitrile, are shown in Fig. 10, further demonstrating that a significant compositional gradient was achieved using the technique of controlled monomer addition.[28]

Work done by Sawamoto and co-workers with styrene and methyl methacrylate has shown an interesting modification of the semi-batch process.[32] In this report, random copolymerization of styrene and methyl methacrylate is allowed to progress to 52% conversion of styrene, at which point an additional aliquot of methyl methacrylate monomer is added. The copolymerization is allowed to progress further, to 89% conversion of styrene; at which time another aliquot of methyl methacrylate is added. This results in what is essentially a triblock copolymer, in which each of the three blocks is a copolymer of styrene and methyl methacrylate containing different compositions of the two monomers. The composition should change along the chain in the second and third blocks owing to the changing composition of monomer feed.

PHYSICAL PROPERTIES OF GRADIENT COPOLYMERS

One of the main motivations for the study of gradient copolymers is the possibility that gradient copolymers should have physical properties which differ considerably from those of block or random copolymers with analogous compositions. Various composition distributions of specifically interacting comonomers along chains should lead to variation of possibilities and scales of the spatial organization of comonomers and consequently to various properties.

The uniqueness of the physical properties of gradient copolymers is seen in the DSC thermograms shown in Fig. 11,[58] which indicates the glass transition regions of a diblock, random and gradient copolymers, all containing similar final cumulative monomer compositions of styrene and methyl acrylate. As expected, the block copolymer shows two distinct glass transitions corresponding to the T_g of polystyrene ($T_g \approx 100\,°C$) and that of poly(methyl acrylate) ($T_g \approx 10\,°C$), and the random copolymer shows a single glass transition ($T_g \approx 75\,°C$, between the two T_g values of the corresponding homopolymers. This indicates that the block copolymer exists in a strongly microphase segregated state whereas the random copolymer exists as a single-phase system. The thermodynamic behavior of the gradient copolymers, however, is more complicated. Figure 11 shows two thermograms for the gradient copolymer samples obtained by different thermal treatment: (1) the rapidly cooled sample for which the thermogram indicates one broad glass transition above the T_g of poly(methyl acrylate) and (2) the sample of the same gradient copolymer but annealed above 50 °C for which an additional transition at ~70 °C is observed. This shows that not only is the phase state of the gradient copolymer different from both the random and block copolymer, but also that it is strongly dependent on the thermal history of the sample.[58]

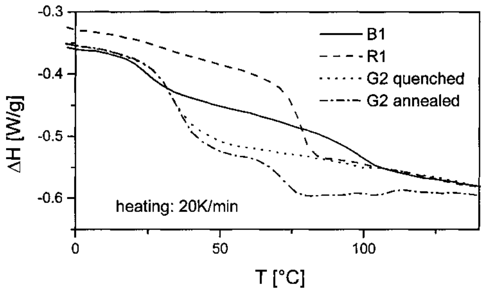


Figure 11. Comparison of DSC thermograms for styrene–methyl acrylate diblock, gradient and random copolymers. Quenched and annealed samples of the gradient copolymers are shown. The block copolymer (B1) contained 40 mol% methyl acrylate and had an M_n value of 16 000 and a polydispersity value of $M_w/M_n = 1.42$. The random copolymer (R1) contained 57 mol% methyl acrylate and had an M_n value of 22 000 and a polydispersity value of $M_w/M_n = 1.18$. The gradient copolymer (G2) contained a final cumulative composition of 57 mol% methyl acrylate and had an M_n value of 12 000 and a polydispersity value of $M_w/M_n = 1.19$

Similar effects are illustrated in Fig. 12, which shows the temperature dependences of the shear moduli (G', G'') for samples of the three copolymers discussed in Fig.

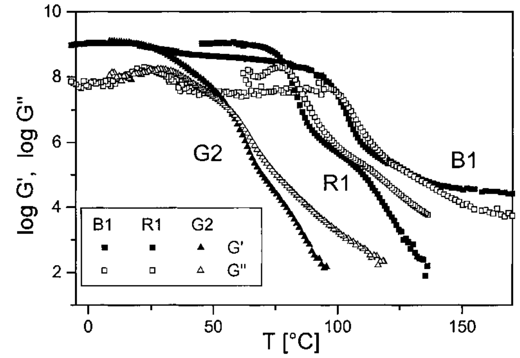


Figure 12. Temperature dependencies of the storage (G') and loss moduli (G'') for styrene–methyl acrylate diblock, gradient and random copolymers. The block copolymer (B1) contained 40 mol% methyl acrylate and had an M_n value of 16 000, and a polydispersity value of $M_w/M_n = 1.42$. The random copolymer (R1) contained 57 mol% methyl acrylate and had an M_n value of 22 000 and a polydispersity value of $M_w/M_n = 1.18$. The gradient copolymer (G2) contained a final cumulative composition of 57 mol% methyl acrylate and had an M_n value of 12 000 and a polydispersity value of $M_w/M_n = 1.19$

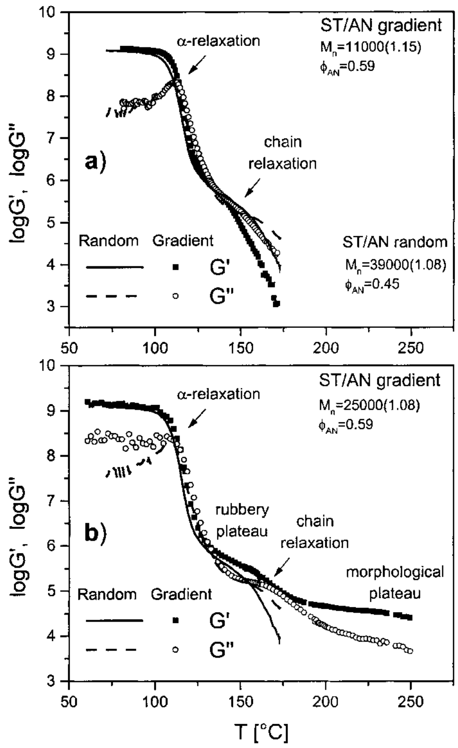


Figure 13. Temperature dependences of the storage (G') and loss moduli (G'') for styrene–acrylonitrile gradient copolymers. Both gradient copolymers contained a final cumulative composition of 59 mol% acrylonitrile and had an M_n value of 11 000 and a polydispersity value of M_w/M_n = 1.15, and an M_n value of 25 000 and a polydispersity value of M_w/M_n = 1.08, as indicated in (a) and (b), respectively. For comparison, results for a random copolymer are shown (M_n = 39 000, M_w/M_n = 1.08, ϕ_{AN} = 0.45)

11.[58] In this figure, it can again be seen that two distinct segmental relaxation processes are present in the diblock copolymer whereas only one is seen for the random copolymer. For the gradient copolymer, one but extremely broad segmental relaxation is seen, indicating a broad concentration distribution related to a continuous composition change in the microphase-separated state of the gradient copolymer.[58]

The above results show that in the case of copolymers consisting of monomers with distinctly different segmental mobilities, the variation of composition profiles along copolymer chains can lead to considerable differences in the physical behavior related to the main softening transition in the material.

Similar studies of the physical properties have been conducted also for the gradient copolymers of styrene and acrylonitrile, i.e. copolymers consisting of monomers which form homopolymers having almost the same glass transition temperatures. The results of dynamic mechanical testing of a styrene–acrylonitrile gradient copolymer are displayed in Fig. 13. In this specific case, various distributions of comonomers in chains do not involve remarkable changes in segmental mobilities, i.e. in the position of the α-relaxation transition on the temperature scale. The transition remains at almost the same temperature for block, random and gradient copolymers. The storage (G') and loss (G'') moduli presented for the two gradient copolymers, which differ in the molecular weight show, however, distinct differences in behavior at higher temperatures. Both copolymers contain 59 mol% acrylonitrile, sample 1 had M_n = 25 000 with a polydispersity of M_w/M_n = 1.08, while sample 2 had M_n = 11 000 with a polydisperity of M_w/M_n = 1.15. For the polymer with the smaller molecular weight, the typical flow regime is observed above 150 °C which probably indicates a homogeneous melt state, whereas for the high molecular weight polymer the long high-temperature plateau suggests the microphase separation still existing in this temperature range in the gradient copolymer.

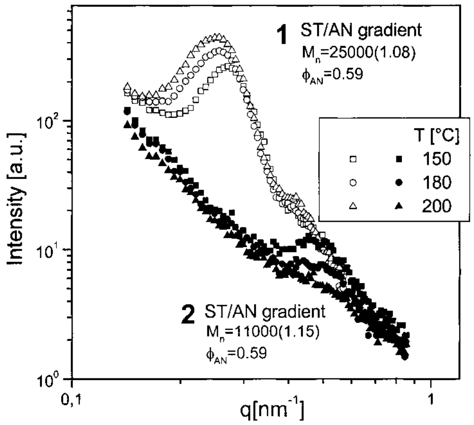


Figure 14. Small-angle x-ray scattering of two gradient copolymers. Both copolymers contained 59 mol% acrylonitrile, gradient 1 had M_n = 25 000 and M_w/M_n = 1.08, and gradient 2 had M_n = 11 000 and M_w/M_n = 1.15

The above conjectures have been confirmed by the structural evidence obtained from the small-angle x-ray scattering. Figure 14 shows the results of small-angle x-ray scattering for samples of the two above gradient copolymers differing only in total molecular weight. In examining the results for the two gradient copolymers, it is observed that both samples show the periodicity depending on molecular weight. The higher molecular weight sample displayed a periodicity of 22.4 nm, and the lower molecular weight sample had a periodicity of 13.4 nm. The higher molecular weight sample stayed in the phase-separated regime at temperatures above 200 °C. For the lower molecular weight sample, however, the order decreased with increasing temperature and a single phase was formed at temperatures above 150 °C. This indicates that it is possible to manipulate phase transitions by changing molecular weights and, perhaps, compositions and the shape of the gradient.

It can be seen in Figs 11–14 that gradient copolymers do, in fact, exhibit thermal and mechanical properties that are different from those of both block and random copolymers. This difference in mechanical properties is

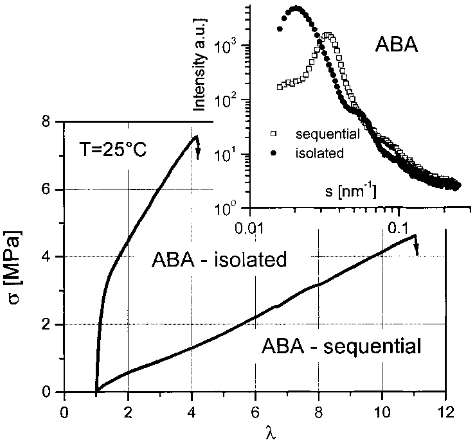


Figure 15. Stress–strain curves recorded for the two triblock copolymer samples during cold drawing of films with a constant rate of 1 min^{-1}. ABA-isolated sample was a clean triblock, with an $M_n = 65\,200$ central block of *n*-butyl acrylate, two blocks of methyl methacrylate with $M_n = 13\,150$ and an overall polydispersity of $M_w/M_n = 1.34$. ABA-sequential contained a clean central block of *n*-butyl acrylate of $M_n = 67\,500$ and two end blocks which were gradient copolymers containing 13 mol% *n*-butyl acrylate and 87 mol% methyl methacrylate, with $M_n = 10\,600$ and an overall polydispersity of $M_w/M_n = 1.24$. The insert shows the small-angle x-ray scattering intensities for these samples

also demonstrated in Fig. 15, which shows an example of tensile testing on two ABA triblock copolymers, both of which contain a clean central block of poly(*n*-butyl acrylate), with M_n values of 65 200 and 67 500. One of the samples had two clean poly(methyl methacrylate) end blocks ($M_n = 13150$), the other sample had two end blocks which were methyl methacrylate–*n*-butyl acrylate gradient copolymers (13 mol% *n*-butyl acrylate and $M_n = 10600$). It can be seen that the addition of gradient nature to the end blocks of the triblock copolymer led to reduced ultimate stress but much longer elongations at break-even in the case when for both samples the microphase separated state was observed by means of the small-angle x-ray scattering (see the inset).[59]

Since gradient copolymers are chemically anisotropic, they may be useful as compatibilizers for immiscible polymer blends. Copolymers compatibilize blends by acting as large surfactants, decreasing the interfacial tension at an immiscible interface.[60] The ability of a copolymer to reduce interfacial tension depends on the orientation of the copolymer at the interface. In turn, for linear chains, this orientation is a strong function of instantaneous composition. Block copolymers orient orthogonal to the interfacial surface, extending into regions of both homopolymers. In contrast, random copolymers localize at the interface but may weave in and out of each component of the blend, with little extension into homopolymer domains. Since gradient copolymers combine structural characteristics of block and random copolymers, their orientation at an interface may be between these two extremes. Consequently, gradient copolymers may be able to compatibilize an interface almost as efficiently as block copolymers, but at a significantly lower cost.

Various aspects of simulated behavior relating to the compatibilizing ability of gradient, random, and diblock copolymers are shown in Fig. 16, which points to the conclusion that for most aspects of compatibilizing behavior, the behavior of gradient copolymers lies somewhere between those of the random and block copolymers. As seen in Fig. 16(a),[58] both the random and gradient copolymers give broader concentration profiles that are close to the virtual homopolymer interface. Figure 16(b) shows that all of the copolymers suppress non-uniformity in the distribution of centers of mass of the polymer chains with the block copolymer showing the strongest effect, but a significant reduction in chain orientation preference is only seen for block and gradient copolymers, as shown in Fig. 16(c). Figure 16(d) shows that the gradient copolymer is the most effective in reducing non-uniformity in the distribution of chain ends. Figure 16(e) demonstrates that the gradient copolymer has an intermediate position between block and random copolymer on affecting the contacts between two phases along the direction perpendicular to the interface. The results in Fig. 16 show that gradient copolymers should be as effective as block copolymers in compatibilizing polymer blends but with an additional advantage of stronger reduction of various heterogeneities (chain ends, orientations) which might influence the mechanical strength of the interfaces. However, their concentration at the interface may be higher than that of the block copolymers, which may form micelles and reverse micelles in both of the homopolymers.

FUTURE DIRECTIONS OF THE STUDY OF GRADIENT COPOLYMERS

Gradient copolymers form a novel class of materials that only came into existence with the advent of living polymerization techniques. As yet, the field of gradient copolymers has not been thoroughly explored, and there is much opportunity for research into the synthesis of gradient copolymers and the characterization of their unique physical properties. ATRP and other CRP techniques are perhaps the most attractive methods for the synthesis of gradient copolymers owing to the convenience and versatility of these techniques and the facile cross-propagation that these techniques exhibit.

Both the physical properties of gradient copolymers and the mechanistic aspects of their synthesis must be further studied in order to understand fully the advantages and limitations of this class of materials.

Further information on the rheological, mechanical and thermal properties of gradient copolymers must be collected before all of the possible applications of these

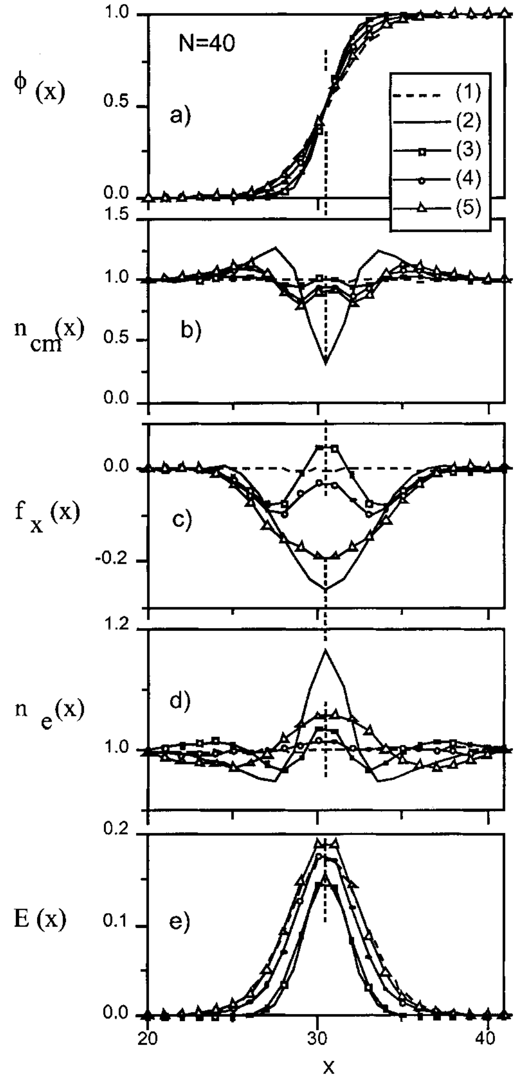


Figure 16. Distributions of (a) concentration, (b) centers of mass of polymers, (c) orientation factor of chain end-to-end vectors with respect to the normal to the interface, (d) chain ends and (e) A–B contacts along a direction perpendicular to the interface (*x* distance, in units of lattice constant, along this direction). Various interfaces are considered: (1) a virtual interface in a homopolymer, (2) A–B interface of strongly incompatible polymers and (3), (4) and (5) A–B interfaces modified with diblock, gradient and random copolymers, respectively

materials can be determined. Additionally, there are currently no convenient or effective methods of directly measuring sequence distribution of monomer units in a gradient copolymer.[25] Developing methods to analyze the microstructure of these copolymers better would allow for a more complete understanding of the relationship between microstructure and the physical properties of the materials.

Properly understanding gradient copolymers will also require a more complete understanding of the mechanism of these copolymerizations. One particular mechanistic aspect of these copolymerizations is the effect of the dynamics of the exchange between active and dormant species in a living polymerization. It is known that the dynamics of this exchange has a strong effect on the control of molecular weight and molecular weight distribution in a controlled/living polymerization,[7] but it is not entirely clear how it influences the gradient in composition of a copolymer.

Preliminary results on the physical properties of these materials indicate that their properties will warrant a great deal of study. In addition to the unique mechanical, thermal and optical properties of these materials, it also appears that gradient copolymers might be useful as blend compatibilizers. The field of gradient copolymers has not yet been studied extensively enough to realize the full potential of these materials.

Acknowledgements

The financial support of the NSF, EPA and the industrial members of the ATRP Consortium is gratefully acknowledged.

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