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Stereogradient Polymers Formed by Controlled/Living Radical Polymerization of Bulky Methacrylate Monomers**

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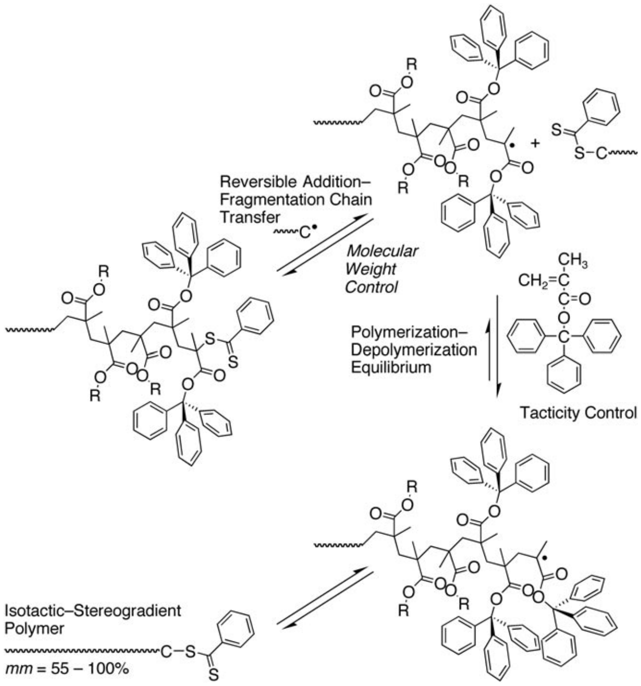
The stereochemistry of monomer additions can be recorded on a living polymer chain because the chain continues its growth throughout the polymerization process. If the stereochemistry of the monomer addition can be changed during the living polymerization, it will be reflected accordingly in the changes in the tacticity along the chain. However, unless the chain is living, the products will only be mixtures of the polymer chains with different tacticities and various chain lengths.

A stereogradient polymer is defined as a polymer in which the tacticity gradually varies along the chain, and is of interest because of the continuous changes in its physical and thermal properties. This type of stereocontrolled polymer is rather new, with only a few examples reported to date;[1–3] this is partly because the synthetic methodology requires both living and stereospecific polymerization and also requires a steady change in the stereospecificity.

A methacrylate monomer with extremely bulky pendant groups, such as triphenylmethyl (TrMA) and its analogues, undergoes anionic polymerization to give highly isotactic polymers.[4,5] Furthermore, asymmetric anionic polymerizations with chiral initiators afford optically active polymers with a stable one-handed helical conformation,[6,7] which are commercialized as a chiral support for HPLC.[8] Even radical polymerizations generate isotactic-rich polymers because of steric repulsion between the bulky ester groups of an incoming monomer and of the growing chain end, which results in a rigid helical conformation of the polymer chain maintained by the bulky substituents, although the isotacticity is slightly lower than for anionic polymerizations.[4] The isotacticity (*mm*) of poly(TrMA) obtained by radical polymerization ranges from 64 % to 99 % and is dependent on the monomer concentrations, temperatures, and solvents, which is most probably due to changes in the kinetic and thermodynamic control.[9] In particular, the isotacticity increases with the decreasing monomer concentration, which suggests the possibility of preparing stereogradient polymers by giving the chains a living nature (Scheme 1).



Scheme 1. Stereogradient polymer by RAFT polymerization of triphenylmethyl methacrylate.

We thus investigated the controlled/living radical polymerization[10] of TrMA by using reversible addition–fragmentation chain transfer (RAFT) agents with varying monomer concentrations, temperatures, and solvents for the spontaneous formation of the stereogradient polymers. TrMA was polymerized by using 2,2′-azobisisobutyronitrile (AIBN) in the presence of cumyl dithiobenzoate (CDB)[11] at 60 °C. The polymerization occurred smoothly and proceeded at almost the same rate for methyl methacrylate (MMA) under the same conditions (see Figure S1 in the Supporting Information). The size-exclusion chromatograms (SEC) of the poly(TrMA) showed broad and bimodal molecular weight distributions (MWDs; dotted SEC curves in Figure 1) because of the aggregation of the rigid and less soluble polymers,[12] which were then converted into poly(MMA) by acid hydrol-

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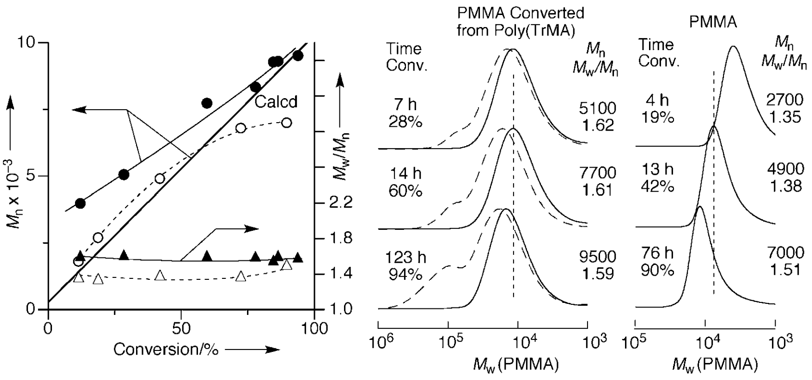

Figure 1. M_n, M_w/M_n, and SEC curves of poly(MMA) obtained from the RAFT polymerization of TrMA (●, ▲) and MMA (○, △) with CDB/AIBN in toluene at 60 °C: $[M]_0 = 1.0$ M; $[M]_0/[CDB]_0/[AIBN]_0 = 100:1:0.5$. The diagonal line indicates the calculated M_n, assuming the formation of one polymer chain per CDB molecule. The dotted SEC curves are elution diagrams of poly(TrMA).

ysis of the trityl group, followed by methylation with trimethylsilyl diazomethane. The obtained poly(MMA) showed unimodal SEC curves, and the number-average molecular weights (M_n) increased with the conversion and were very close to the calculated values. Slightly broader MWDs suggest a slower addition-fragmentation process for this bulky monomer. Trithiocarbonate-type RAFT agents also enabled a similar molecular weight control (Figure 2). Thus, the controlled/living radical polymerization of TrMA was attained by using these RAFT agents.

The tacticity was measured from the ^{1}H or ^{13}C NMR spectra of the poly(MMA) obtained from poly(TrMA) (Figure S2 in the Supporting Information). All the polymers showed a predominant isotacticity, which increased with the consumption of TrMA. The entire or cumulative triad isotacticity (mm_{cum}) obtained for each conversion increased from approximately 55 % to 65 %. Figure 2 shows a plot of the mm_{cum} value against the normalized chain length, that is, the chain length of the polymers obtained for each conversion relative to those at the final conversions. The mm_{cum} values depended on the monomer conversion, but were almost independent of the structure of the RAFT agents. The isotactic contents (mm_{inst}) for a certain part in the chains were then calculated from the differential increase in the mm_{cum} value versus the chain length. The instantaneous values of the isotacticity (mm_{inst}) gradually increased with the normalized chain lengths from 55 % to finally over 95 % (Figure 2), which indicates the formation of isotactic-rich stereogradient polymers. This means that a decrease in the monomer concentration changes the propagation into a more isotactic enchainment.

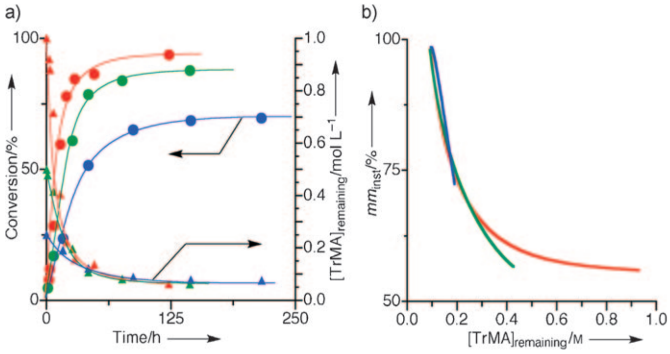

Figure 3. Effects of initial monomer concentrations on the accessible conversion (a) and instantaneous *mm* triad contents (b) in the RAFT polymerizations of TrMA in toluene at 60 °C: $[TrMA]_0 = 1.0$ (●, ▲, ——), 0.50 (●, ▲, ——), and 0.25 (●, ▲, ——) M; $[TrMA]_0/[CDB]_0/[AIBN]_0 = 100:1:0.5$.

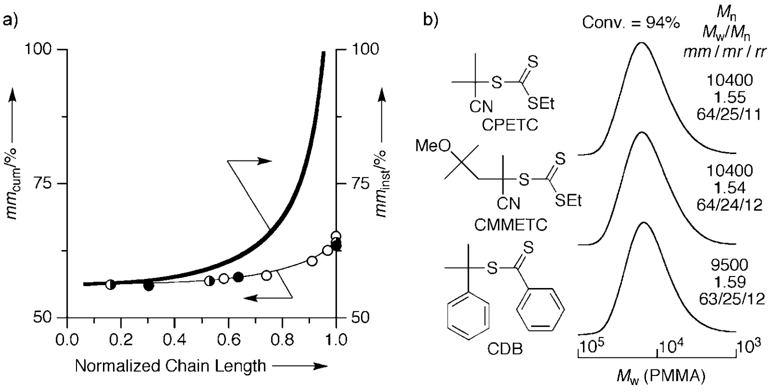

Figure 2. Dependences of cumulative and instantaneous *mm* triad contents on the normalized chain length (a) and SEC curves of poly(MMA) (b) from the RAFT polymerizations of TrMA in toluene at 60 °C; $[TrMA]_0 = 1.0$ M. $[TrMA]_0/[RAFT\ agent]_0/[AIBN]_0 = 100:1:0.5$; RAFT agent: 2-cyanoprop-2-yl ethyl trithiocarbonate (CPETC; ◑), 2-cyano-4-methoxy-4-methylpentan-2-yl ethyl carbonotrithioate (CMMETC; ○), and CDB (●).

The effects of the monomer concentration on the polymerization were then investigated with CDB in toluene at 60 °C. Upon decreasing the initial monomer concentrations, polymerizations became slower and the final conversions became lower (Figure 3 a). However, the final monomer concentrations reached almost the same value (60–70 mM) independent of the initial concentrations, which indicated the presence of the equilibrium monomer concentration for such a bulky monomer even at 60 °C.[13] In all cases, the molecular weights increased with the conversion, which shows that the molecular weight control is achievable irrespective of the monomer concentrations (see Figure S3 a in the Supporting Information).

The instantaneous isotacticity value (mm_{inst}) also increased as the monomer conversion increased and was higher for a lower initial monomer concentration at the same monomer conversion (see Figure S3 b in the Supporting Information). Plots of mm_{inst} versus the remaining monomer concentration for different values of initial monomer concentration practically follow the same curve, which gradually increased as the instantaneous monomer concentration decreased (Figure 3b). These results indicate that the tacticity is governed by the remaining monomer concentration.

The effects of the temperature were also examined on the polymerizations. Upon raising the temperature, the initial polymerization rate increased while the final monomer conversions became lower. The mm_{inst} value increased with temperature (see Figure S4 in the Supporting Information). These results suggest that lowering the monomer concentration or increasing the polymerization temperature makes the formation of the more thermodynamically stable isotactic propagating chain ends more favorable by the reversible polymerization–depolymerization equilibrium.

The polymerization–depolymerization equilibrium was further examined by increasing the temperature during the polymerization. We first conducted the RAFT polymerization at 60 °C and increased the temperature to 80 °C when the conversion reached 70 %. Upon increasing the temperature, the monomer conversion decreased and remained constant at around 60 % (see Figure S5 in the Supporting Information). The molecular weights also decreased and became constant while the molecular weight distributions became broader. This result also supports the presence of the polymerization–depolymerization equilibrium by the reversible formation of the growing radical species.

We then measured the final accessible monomer conversions by varying the temperatures (40–100 °C) and the initial monomer concentrations (0.25–1.0 M) to obtain the equilibrium monomer concentration ($[M]_{\text{eq}}$) at each temperature (see Table S1 in the Supporting Information). We plotted the logarithmic monomer concentrations versus the reciprocal of the temperatures (Figure 4). The plot showed a good linear relationship, which indicated the propagation–depropagation equilibrium for this α-substituted bulky monomer. The enthalpy (ΔH_p) and entropy (ΔS_p) values for the polymerizations of TrMA were calculated from this linear plot ($\ln[M]_{\text{eq}} = \Delta H_p/RT - \Delta S_p/R$), which yielded values of $\Delta H_p = -60.4\ \text{kJ mol}^{-1}$ and $\Delta S_p = -160.5\ \text{J mol}^{-1}\text{K}^{-1}$.[14] The enthalpy value is almost the same as those of other methacrylate monomers ($\Delta H_p(\text{MMA}) = -56\ \text{kJ mol}^{-1}$, ΔH_p(ethyl methacrylate) $= -60\ \text{kJ mol}^{-1}$) while the entropy value is higher ($\Delta S_p(\text{MMA}) = -118\ \text{J mol}^{-1}\text{K}^{-1}$, ΔS_p(ethyl methacrylate) $= -124\ \text{J mol}^{-1}\text{K}^{-1}$), probably because of the rigid main-chain conformation of poly(TrMA).[15] The linear plot also gave the ceiling temperature value of TrMA as 104 °C at $[M]_0 = 1.0$ M. This is also reasonable because almost no polymers were obtained at 100 °C for $[M]_0 = 1.0$ M.

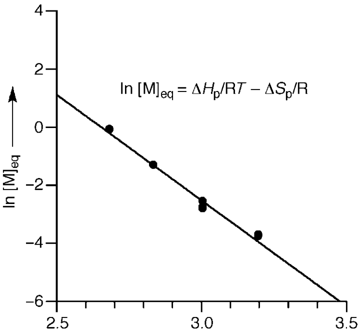

Figure 4. Dependence of equilibrium monomer concentration ($[M]_{\text{eq}}$) on temperature in the RAFT polymerizations of TrMA in toluene.

We further utilized the unique isotactic-rich stereogradient RAFT polymerization for a block copolymerization to synthesize another novel stereocontrolled polymer. Thus we first polymerized MMA with CDB to prepare the syndiotactic-rich living poly(MMA) with RAFT moieties at the chain ends and then employed it as a macroinitiator for the RAFT polymerization of TrMA (Figure 5). After the copolymerization, we converted the trityl substituent into a methyl group and obtained the homopoly(MMA) with narrow MWDs. The cumulative and instantaneous *mm* contents versus the normalized chain length are also shown in Figure 5. The isotacticity was abruptly changed at the blocking point, after which it gradually increased along the chain. The differential spectrum of these polymers also indicates the formation of the isotactic-rich segments in the second polymerization (cumulative *mm*/*mr*/*rr* = 61:26:13; see Figure S6 in the Supporting Information). These show the formation of the stereoblock PMMA[16] with syndiotactic and isotactic-stereogradient segments.

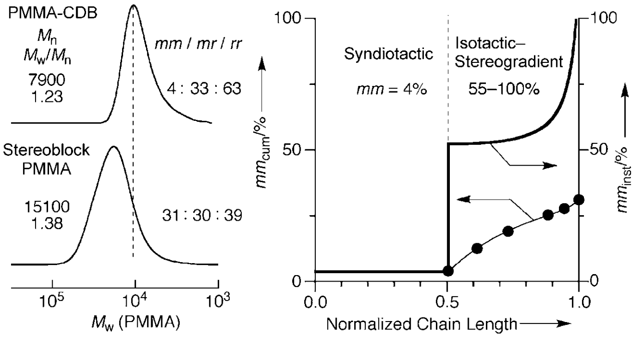

Figure 5. Stereoblock poly(MMA) obtained from the RAFT block copolymerization of MMA and TrMA in toluene at 60 °C. For poly(MMA) macroinitiator: $[\text{MMA}]_0 = 7.0$ M, $[\text{AIBN}]_0 = 5.0$ mM, $[\text{CDB}]_0 = 35$ mM; for poly(MMA-*b*-TrMA): $[\text{TrMA}]_0 = 1.0$ M, $[\text{AIBN}]_0 = 6.0$ mM, $[\text{PMMA-CDB}]_0 = 12$ mM.

In conclusion, we have demonstrated the formation of stereogradient polymers by RAFT polymerization of a bulky methacrylate monomer, in which the isospecificity gradually increased with a decrease in the monomer concentrations. This is caused by the propagation–depropagation equilibrium, which can convert a less stable growing polymer terminal with the *r* conformation into the more stable *m* form especially at a lower monomer concentration. Further studies are now directed to the controlled/living radical copolymerization of bulky methacrylates with other monomers for the synthesis of novel stereocontrolled polymers.[17]

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[17] The synthesis of highly isotactic poly(methacrylates) with controlled molecular weights was attempted whereby the TrMA concentration was kept low by slow monomer addition from a syringe pump, but it was experimentally difficult to attain appropriate conditions mainly because of a very slow polymerization under the equilibrium monomer concentration.