Controlled/Living Radical Polymerization of *tert*-Butyl Acrylate Mediated by Chiral Nitroxides. A Stereochemical Study

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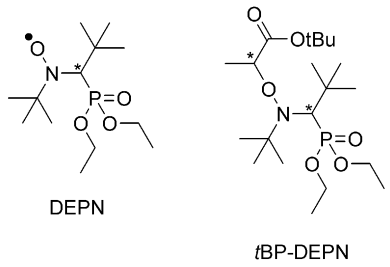
ABSTRACT: The two diastereomeric alkoxyamines of *t*BP-DEPN, where *t*BP is 1-(*tert*-butoxycarbonyl)-ethyl and DEPN is *N*-(2-methylpropyl)-*N*-(1-diethylphosphophono-2,2-dimethylpropyl)aminoxyl, have marked differences in their thermodynamic stability (ratio of diastereomers is 5:1 at 100 °C in *o*-dichlorobenzene). They were used as initiators for the controlled/living radical polymerization of *tert*-butyl acrylate to test the premise that such moderators could potentially affect the tacticity of the resulting poly(*tert*-butyl acrylate). 2D NMR was used to analyze the end group configuration for the samples with shorter chain lengths ($DP_n = 15-20$). Although the diastereomeric excess in the polymer alkoxyamine end group is even higher than for the model compound (ratio of diastereomers is 7:1), the distribution of terminal triads in poly(*tert*-butyl acrylate) does not differ from those in the entire chain and is identical to that of the polymers prepared by ATRP. Thus, the tacticities of the poly(*tert*-butyl acrylate)s prepared by DEPN-mediated polymerization, atom transfer radical polymerization (ATRP), and conventional free radical polymerization were the same.

Introduction

Controlled/living radical polymerization (CRP) has recently became a powerful synthetic tool for the preparation of polymers with predetermined molecular weight, low polydispersity, controlled composition, topology, and functionality.[1−3] The three most widely used methods of CRP, in academic and industrial research, are nitroxide-mediated polymerization (NMP),[4,5] atom transfer radical polymerization (ATRP),[6−8] and degenerative transfer processes,[9,10] especially reversible addition−fragmentation chain transfer (RAFT).[11] Control of polymer tacticity however remains an important challenge for free radical polymerization.[12,13] Stereocontrol of (meth)acrylates would provide commercially important polymers with entirely new properties. However, such control has only been achieved in anionic and coordination polymerizations.[14] In the free radical polymerization of many commercially important monomers the planarity of the generated radicals (sp^2 hybridization) prevents control of polymer tacticity. Several successful attempts to control tacticity have been reported: one route is based on an auxiliary group approach[15] and another on complexation of monomers with either protic compounds or Lewis acids.[13,16] Stereocontrol may also be enhanced in template polymerization or polymerization processes conducted in a confined space or within inclusion complexes.[17,18] Several unsuccessful attempts have been reported using CRP methods based on chiral nitroxides[19] and chiral ligands in ATRP.[20] The failure to control tacticity in these systems was, at least partially, ascribed to the insufficient chiral control by the capping agent.

In this paper we report the results of CRP of *tert*-butyl acrylate (*t*BA) using alkoxyamines with much stronger stereoselection, resulting from a 5:1 preference for one of the diastereomers in the corresponding model alkoxyamine at 100 °C. Previous studies had employed nitroxides with much weaker stereoselection (<3:1).[19,21] The chiral nitroxide used in this work, *N*-(2-methylpropyl)-*N*-(1-diethylphosphono-2,2-dimethylpropyl)aminoxyl radical (named DEPN or SG1)[22] (Scheme 1), is among the most useful mediators for CRP, especially for acrylates.[23−28] Scheme 1 presents structures of both DEPN and the alkoxyamine *t*BP-DEPN.

Scheme 1. Structures of DEPN and TBP-DEPN



Experimental Section

Materials. Cu(I)Br (98%, ACROS) was purified by stirring in glacial acetic acid overnight, then washing with ethanol and diethyl ether, and drying under a nitrogen atmosphere. *tert*-Butyl 2-bromopropionate (*t*BBP, 97+%, TCI), dimethyl 2,6-dibromoheptanedionate (97%, Aldrich), pentamethyldiethylenetriamine (PMDETA, 99%, Aldrich), and 2,2′-azobis(2-methylpropionitrile) (AIBN, 98%, Kodak) were used without purification. All other chemicals were used as received. *N*-(2-Methylpropyl)-*N*-(1-diethylphosphophono-2,2-dimethylpropyl)-aminoxyl (DEPN, 92%) was provided by Atofina. The synthesis of 1,1,3,3-tetramethylisoindolin-*N*-oxyl (TMIO) has been as described in ref 29 (cf. Scheme 2)

tert-Butyl 2-(N-(2-methylpropyl)-N-(1-diethylphosphophono-2,2-dimethyl-propyl)aminoxy)propionate (*t*BP-DEPN adduct) was synthesized in a manner similar to the procedure described in ref 25. A mixture of 0.209 g (1 mmol) of *t*BBP, 1 mmol of CuBr/PMDETA complex (prepared from 0.143 g (1 mmol) of CuBr and 0.173 g (1 mmol) of PMDETA in 10 mL of acetone), 0.177 g (0.6 mmol) of DEPN, and 0.064 g (1 mmol) of Cu(0) were stirred in 25 mL of acetone at 40 °C for 20 h. The reaction mixture was diluted to 50 mL by addition of diethyl ether, filtered, and passed through a short column of alumina to remove the Cu(II) complex. Solvents and unreacted

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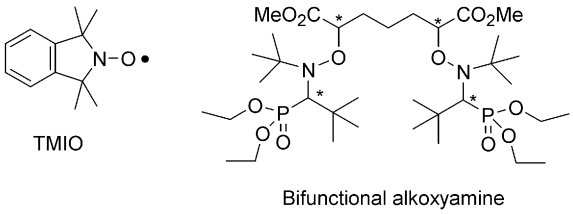
Scheme 2. Structures of TMIO and Bifunctional Alkoxyamine



bromoester were removed under vacuum. The major isomer of the alkoxyamine was isolated by column chromatography on silica gel with hexane/ethyl acetate, 1/1; yield 0.112 g (44%). ^{1}H NMR indicates the diastereomeric purity of 90%, i.e., higher than the equilibrium ratio at 100 °C. ^{1}H NMR (300 MHz, $CDCl_3$, major isomer, expected configuration is (R,R) and (S,S) according to the similarity of NMR spectra with those reported in ref 30): 4.41 (q, 2H, $^3J_{H-H} = 7.1$ Hz, C*H*−ON), 4.3−3.8 (m, 4H, 2CH_2−O), 3.25 (d, 1H, $^2J_{H-P} = 25.0$ Hz, C*H*−P), 1.46 (d, 3H, $^3J_{H-H} = 7.1$ Hz, CH_3), 1.44 (s, 9H, (CH_3)$_3$C−O), 1.27 (br t, 6H, 2CH_3), 1.14 (s, 9H, (CH_3)$_3$C), 1.12 (s, 9H, (CH_3)$_3$C−O); (300 MHz, $CDCl_3$, minor isomer, expected configuration is (R,S) and (S,R)): 4.54 (q, 2H, $^3J_{H-H} = 7.0$ Hz, C*H*−ON), 4.3−3.8 (m, 2CH_2−O), 3.33 (d, 1H, $^2J_{H-P} = 27.0$ Hz, C*H*−P), 1.45 (d, 3H, $^3J_{H-H} = 7.0$ Hz, CH_3), 1.43 (s, 9H, (CH_3)$_3$C−O), 1.27 (br t, CH_3), 1.25 (br t, CH_3), 1.15 (s, 9H, (CH_3)$_3$C), 1.12 (s, 9H, (CH_3)$_3$C).

Dimethyl 2,6-Bis(N-(2-methylpropyl)-N-(1-diethylphosphono-2,2-dimethyl-propyl)aminoxy)heptanedionate. A solution of 2.08 g (12 mmol) of PMDETA in 10 mL of benzene was degassed by three freeze−pump−thaw cycles and transferred by syringe to a flask contained 1.72 g (12 mmol) of CuBr and purged by nitrogen. After the Cu(I) complex formed (ca. 20 min), the solution was added to a degassed mixture of 2.08 g (6 mmol) of dimethyl 2,6-dibromoheptanedionate, 3.54 g (12 mmol) of DEPN, and 0.76 g (12 mmol) of Cu (0) in 10 mL of benzene. After stirring for 3 h at 45 °C and 2 h at 55 °C, the mixture was filtered, diluted with ethyl acetate, filtered again, and passed through a short column of neutral alumina (eluent ethyl acetate). Evaporation of the solvent gave yellow viscous oil (4.51 g, 97%) which mainly contained the targeted product (by NMR) as well as some free SG1 (HPLC) and Cu complex. Chromatography on a short column of alumina with ethyl acetate/petroleum ether, 3/1 as eluent, gave 3.52 g (76%) of the targeted product (number of isomers) free from DEPN as monitored by HPLC. ^{1}H NMR (300 MHz, $CDCl_3$, mixture of isomers): 4.5−4.3 (br, 2H, 2C*H*−ON), 4.3−3.8 (br, 8H, 4CH_2−O), 3.65 (few singlets, 6H, 2CH_3−O), 3.33 (br d, 2H, $^2J_{H-P} \sim$ 26 Hz, C*H*−P), 2.1 (br, 4H, 2CH_2), 1.65 (br, 2H, CH_2), 1.35−1.2 (few triplets, 12H, 4CH_3), 1.18−1.02 (few singlets, 36H, 4(CH_3)$_3$C) (cf. Scheme 2).

Polymerization. *Sample 1.* A mixture of 0.120 g (0.730 mmol) of AIBN, 0.443 g (1.39 mmol) of DEPN, and 10 mL (70 mmol) of *tert*-butyl acrylate was deoxygenated by bubbling with nitrogen for 30 min. The reaction mixture was placed in an oil bath at 120 °C and stirred for 1.5 h at this temperature. After cooling, excess *t*BA was removed under vacuum, the residue was dissolved in THF, and the formed solution was slowly poured under stirring into a cold (∼−15 °C) methanol/water mixture, 1/1 vol, to precipitate the polymer. GPC analysis of the product gave $M_n = 2000$, which corresponds to ca. 14% monomer conversion; $M_w/M_n = 1.16$.

Sample 2 was prepared by ATRP polymerization of *t*BA under conditions similar to those described in ref 31 using 0.061 g (0.18 mmol) of *tert*-butyl 2-bromopropionate as the initiator. Other reagents—0.025 g (0.18 mmol) of CuBr, 0.030 g (0.18 mmol) of PMDETA, 0.002 g (0.009 mmol) of $CuBr_2$, 10 mL (70 mmol) of *t*BA, and 2.5 mL of acetone—were added to the mixture prior to reaction. Polymer was isolated after 5 h of reaction at 60 °C. $M_n = 2300$, which corresponds to ca. 5% monomer conversion; $M_w/M_n = 1.27$.

Sample 3 was prepared in a manner similar to sample 1. Reaction time was 5 h at 120 °C; $M_n = 5400$, which corresponds to ca. 40% monomer conversion; $M_w/M_n = 1.18$.

Sample 4 was prepared by ATRP polymerization of *t*BA as described in ref 31 using methyl 2-bromopropionate as the initiator. The reaction time was 5 h at 60 °C. $M_n = 6400$, which corresponds to >90% monomer conversion; $M_w/M_n = 1.13$.

Sample 5. A mixture of 60 mg (0.14 mmol) of *t*BP-DEPN adduct (initial diastereomers ratio 9/1), 9 mg (0.03 mmol) of DEPN, and 8.0 mL (56 mmol) of *t*BA was deoxygenated by bubbling with nitrogen for 30 min. Polymerization was carried out at 120 °C for 6 h. Polymer was purified by precipitation from methanol/water mixture, 1/1 vol, as described for sample 1; $M_n = 24\,800$, which corresponds to ca. 45% monomer conversion; $M_w/M_n = 1.21$.

Sample 6. A mixture of 5.75 g (35.0 mmol) of AIBN and 10 mL (70 mmol) of *t*BA in 70 mL of toluene was deoxygenated by bubbling with nitrogen for 30 min. Polymerization was carried out at 60 °C for 1.5 h. Solvent was evaporated in vacuo; the polymer was dissolved in THF and purified by precipitation from 1/1 vol methanol/water mixture as described for sample 1. $M_n = 12\,600$, $M_w/M_n = 3.31$.

Kinetic Measurements. A solution of 25.4 mg (0.060 mmol) of *t*BP-DEPN, 11.4 mg of TMIO (0.060 mmol), and 4.4 mg of biphenyl (internal standard) in 3.0 mL of chlorobenzene (concentrations of the reagents were 20 mM) was carefully degassed using three freeze−pump−thaw cycles. After the first sample (0.2 mL) was taken, the mixture was placed in an oil bath thermostated to 100 °C. Samples were taken using degassed syringes. The consumption of TMIO was determined using reverse-phase HPLC with a Shimadzu LC 10AD pump, a Waters Nova-Pak C18 column (3.9 × 150 mm), and a Waters 486 tunable absorbance detector ($\lambda = 254$ nm) at 35 °C using acetonitrile and water mixture (75:25 vol %) as eluent. The retention times of TMIO, DEPN, chlorobenzene, and biphenyl were 6.0, 6.4, 7.2, and 9.8 min, respectively.

Trapping of 1-*tert*-Butoxycarbonyl-1-ethyl Radicals by DEPN. A solution of 11.8 mg (0.004 mmol) of DEPN and 13.8 mg (0.006 mmol) of Me_6TREN in 1.0 mL of *o*-dichlorobenzene-d_4 was degassed using three freeze−pump−thaw cycles and transferred by syringe to a flask purged with nitrogen and containing 8.6 mg (0.006 mmol) of CuBr. After the Cu(I) complex formed and the mixture became homogeneous, 8.4 mg (0.004 mmol) of *t*BBP was added, and the mixture was stirred at room temperature for 1.5 h. After exposing the mixture to air for 5 min, it was filtered into an NMR sample tube to remove excess Cu(II) complex, which is insoluble in *o*-dichlorobenzene. The first NMR spectrum was measured after ca. 10 min and showed a ca. 1:1 ratio of the diastereomers of tBP-DEPN. Then, the solution was passed through small layer of alumina to remove all Cu(II) complex, degassed by three freeze−pump−thaw cycles, and stirred in an oil bath heated at 100 °C for 18 h. After cooling to room temperature, the second NMR spectrum was measured, and it showed a ca. 5/1 ratio of diastereomers.

Polymer Characterization. Polymer molecular weights were estimated using a GPC system equipped with a Waters WISP 712 autosampler, a Polymer Standards Service columns (guard, 10^2, 10^3, and 10^5 Å), and a Waters 410 RI detector against linear poly(methyl methacrylate) standards in THF (1 mL/min) at 35 °C. Toluene was used as an internal standard.

NMR Measurements. 1D ^{1}H and ^{13}C NMR spectra were measured at room temperature on a GE NMR spectrometer at 300 and 75 MHz, respectively, using 5% solutions of polymers in chloroform-*d*. The signal of residual protons in chloroform (7.24 ppm) and the center peak of chloroform-*d* (77.0 ppm) were used as internal standards for proton and carbon spectra, respectively.

2D-HSQC NMR spectra were measured at 38 °C on a Bruker DRX 600 NMR spectrometer using 10% solutions of polymers in chloroform-*d*. A total of 16 scans were accumulated over 400 t_1 increments with a relaxation delay of 1 s. A sine apodization function was applied to both dimensions prior to Fourier transformation.

Results and Discussion

Model Compound Studies. Model experiments were conducted to obtain information about diastereomeric preference in the decomposition of alkoxyamine and the coupling of corresponding transient and persistent radicals.

The interconversion of diastereomeric alkoxyamines can be described by the following elementary reactions:[30]

$$I_1 \xrightarrow{k_{d1}} R^\bullet + Y^\bullet \quad (1)$$

$$I_2 \xrightarrow{k_{d2}} R^\bullet + Y^\bullet \quad (2)$$

$$R^\bullet + Y^\bullet \xrightarrow{k_{c1}} I_1 \quad (3)$$

$$R^\bullet + Y^\bullet \xrightarrow{k_{c2}} I_2 \quad (4)$$

$$2R^\bullet \xrightarrow{k_t} P \quad (5)$$

Isomers I_1 and I_2 decompose into the corresponding alkyl and nitroxyl radicals with the rate constants k_{d1} and k_{d2}, respectively. Transient alkyl radicals recombine with persistent nitroxyl radical to yield isomers I_1 and I_2 with the rate constants k_{c1} and k_{c2}, respectively. Side reactions such as disproportionation between alkyl and nitroxides can be neglected.[32] Alkyl radicals also decay by self-termination reaction via recombination and/or disproportionation. For simplicity, only the former is considered.

The detailed kinetic analysis for eqs 1−5 was developed in ref 30. Starting with one pure isomeric alkoxyamine, decomposition will result in the planar 1-(*tert*-butoxycarbonyl)ethyl radical (*t*BP), which can recombine with chiral DEPN yielding two diastereomeric alkoxyamines *t*BP-DEPN. The same reaction will occur with the second isomer. Thus, after a certain time, a quasi-equilibrium between two isomers will be reached. This equilibrium constant and isomer ratio will depend only on the ratio of decomposition and coupling rate constants (eq 6).[30]

$$\frac{[I_1]}{[I_2]} = \frac{k_{c1}}{k_{c2}}\frac{k_{d2}}{k_{d1}} \quad (6)$$

A diastereomeric excess upon *recombination* (i.e., only k_{c1}/k_{c2} ratio) of *t*BP and DEPN radicals can be obtained when homolysis is negligible, i.e., if the synthesis of *t*BP-DEPN is conducted at room temperature in a relatively short reaction time. To meet these conditions, we synthesized the alkoxyamine starting from *tert*-butyl 2-bromopropionate using the CuBr/Me_6TREN complex.[33] Previous studies of the activation rate constants for ATRP processes showed that activation of alkyl 2-bromopropionate with this complex is sufficiently fast even at room temperature.[34] Trapping the corresponding 1-(*tert*-butoxycarbonyl)ethyl radical with free DEPN yielded the *t*BP-DEPN adduct after a short time.

The reaction was performed in deuterated *o*-dichlorobenzene in order to monitor the product ratio by NMR without additional purification (chromatography) and to prevent racemization, thereby allowing determination of the true diastereomeric ratio originating from the recombination process. This methodology is similar to the procedures published in ref 21 but does not require any treatment of the reaction mixture. The solvent was chosen to be as close as possible to that used in previous studies of the reaction between 1-(methoxycarbonyl)-ethyl radical and DEPN and in the homolysis of methyl propionate−DEPN adduct.[30,35]

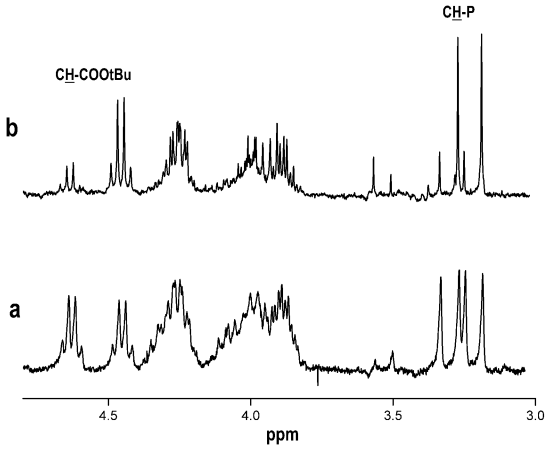


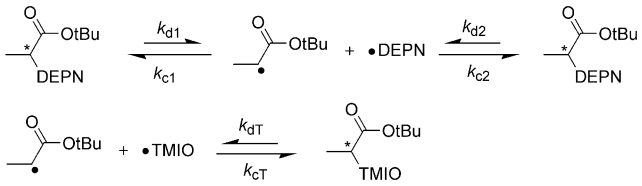
Figure 1. Fragments of ^{1}H NMR spectra of reaction mixture of *t*BBP/CuBr/Me_6TREN/DEPN in *o*-dichlorobenzene: (a) After 1.5 h of the reaction at room temperature, integrated ratio of diastereomers is 1/1; the spectrum shows broad lines due to the presence of paramagnetic Cu^{II} complex in solution. (b) After passing through alumina column (to remove Cu^{II} complex) and stirring overnight at 100 °C; integrated ratio of diastereomers is ca. 5/1.

Figure 1a shows the ^{1}H NMR spectrum obtained immediately after the initial synthesis of the *t*BP-DEPN adduct (cf. Experimental Section) after the excess of insoluble $CuBr_2$/Me_6TREN complex had been filtered off. The diastereomeric ratio (doublets at 3.30 and 3.23 ppm from CH−P groups and quartets at 4.63 and 4.45 ppm from C*H*−O groups in propionate moiety) between the two isomeric alkoxyamines is very close to 1:1. This indicates no stereoselectivity in the coupling process.[36] After the reaction mixture was passed through a small layer of alumina to completely remove the soluble Cu^{II} complex, the mixture was degassed and heated to 100 °C for 18 h. Figure 1b shows the ^{1}H NMR spectrum of the final mixture. The ratio of the integrals of the two doublets (and quartets) is approximately 5:1, quite different from the original 1:1. Further heating of the mixture (110 °C, overnight) did not change the diastereomeric ratio. These results show that while there is no diastereomeric excess upon recombination of 1-(*tert*-butoxycarbonyl)ethyl and DEPN radicals, decomposition of the isomeric alkoxyamines is stereoselective. Similar results were obtained with methyl 2-propionate, although the difference in isomer distribution was much smaller (2.8:1).[30] The diastereomeric excess in the case of either methyl or *tert*-butyl propionate originates from stereoselective cleavage of the alkoxyamines.[30] However, in the case of 1-phenylethyl derivatives, the reported[30] 1.9:1 ratio must arise from selective radical cross-termination, since both diastereomers dissociate with similar rates.[30,34,35]

Accordingly, the diastereomeric excess at equilibrium originates, predominantly, from different decomposition rate constants of the isomeric alkoxyamines (eq 7).

$$\frac{[I_1]}{[I_2]} = \frac{k_{d2}}{k_{d1}} \quad (7)$$

Scheme 3. Reactions Involved in Racemization and Trapping of TBP Radicals with TMIO and DEPN



Therefore, it is sufficient to measure only one k_d (that of the major diastereomer), and the second k_d can be calculated from the above ratio.

We also thermolyzed the major isomer of *t*BP-DEPN, in the presence of a trap for transient radicals. The nitroxide 1,1,3,3-tetramethylisoindolin-*N*-oxyl (TMIO) (cf. Scheme 2), was chosen as the trap due to its expected faster coupling rate constant with *t*BP radical ($k_{cT} \gg k_{c1,2}$, Scheme 3)[37] and also the expected greater stability of the resulting alkoxyamine ($k_{dT} \ll k_{d1,2}$, Scheme 3).[35] It should be noted that coupling between alkyl and nitroxide radicals is usually entropy controlled,[37] and the corresponding rate constants are from 10 to 1000 times smaller than those for diffusion controlled reactions.

If the two conditions ($k_{cT} \gg k_{c1,2}$ and $k_{dT} \ll k_{d1,2}$) are fulfilled, it is not necessary to use an excess of the trap for the experiment. Model calculations show that the decay of the alkoxyamine and of the trap as well as the release of free DEPN and the growth of the adduct tBP-TMIO follows the first-order kinetics in respect to the alkoxyamine concentration until most of the trap is consumed.

Monitoring the decay of the trap (TMIO) or the appearance of free DEPN via HPLC (both nitroxides have large extinction coefficients at 254 nm and their peaks in HPLC can be easily integrated) allows calculation of the decomposition rate constant (cf. Experimental Section). Figure 2 presents the kinetic plots for two alkoxyamines, *t*BP-DEPN and also the bifunctional alkoxyamine (cf. Scheme 2), containing methyl rather than *tert*-butyl groups.

The calculated overall decomposition rate constant $k_d = 2 \times 10^{-4}$ s^{-1} for the mixture of isomers of the bifunctional alkoxyamine in chlorobenzene agrees well with the results reported for the alkoxyamine generated from methyl 2-propionyl radicals with DEPN: $k_{d1} = 1.2 \times 10^{-4}$ s^{-1} (racemic mixture of (R,R) and (S,S) enantiomers) and $k_{d2} = 3.7 \times 10^{-4}$ s^{-1} (racemic mixture of (R,S) and (S,R) enantiomers) in *tert*-butylbenzene[35] or chlorobenzene[30]). However, the decomposition rate constant of the major diastereomer of the *t*BP-DEPN adduct (diastereomeric ratio 9/1, whose expected configuration is (R,R) and (S,S) according to the similarity of NMR spectra with those reported in ref 30) was much smaller: $k_{d1} = 3.0 \times 10^{-5}$ s^{-1}. From the diastereomeric ratio (eq 7), the second rate constant was estimated to be $k_{d2} \approx 1.5 \times 10^{-4}$ s^{-1} assuming that diastereomeric ratios in chlorobenzene and *o*-dichlorobenzene are equal. A comparison of all of these rate constants shows that replacement of the methyl group in the ester moiety by a *tert*-butyl group significantly influences the homolysis rate constants for both diastereomers. The origin of this behavior is presently not clear and requires an additional systematic investigation.

Tacticity of Poly(*tert*-butyl acrylate) Prepared by Different Methods. The relatively large diastereomeric ratio of the alkoxyamines could affect the tacticity

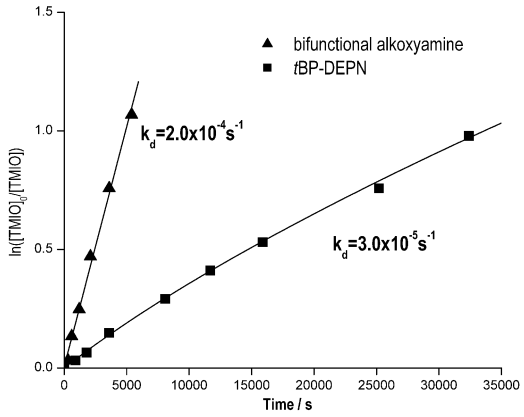


Figure 2. Kinetics of decomposition of dimethyl 2,6-bis(*N*-(2-methylpropyl)-*N*-(1-diethylphosphophono-2,2-dimethyl-propyl)aminoxy)heptanedionate (mixture of diastereomers, cf. Scheme 2) and major diastereomer of *t*BP-DEPN adduct at 100 °C in chlorobenzene by monitoring the decay of free TMIO. The simulation of data for *t*BP-DEPN adduct was performed by taking into account 90% of diastereomeric purity.

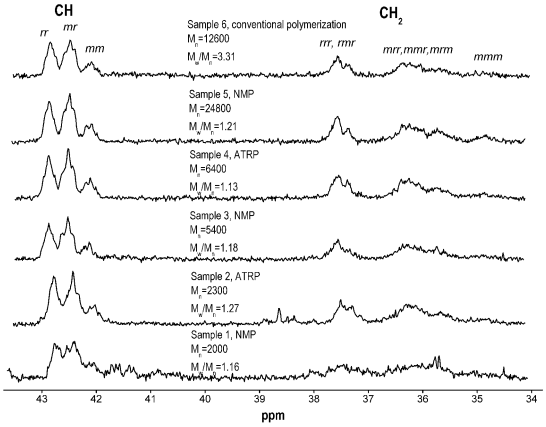


Figure 3. Fragments of ^{13}C NMR spectra (75 MHz) (CH and CH_2 regions) of different samples of poly(*tert*-butyl) acrylate. Assignment of signals is made according to refs 38 and 39.

of poly(*tert*-butyl acrylate) prepared using CRP. Six different samples of poly-*t*BA were prepared; samples 1 and 3 initiated with AIBN/DEPN; sample 5 with diastereomeric *t*BP-DEPN alkoxyamines; two samples by ATRP polymerization, one initiated with methyl 2-bromopropionate (sample 4) and the other with *tert*-butyl 2-bromopropionate (sample 2); and one sample prepared under conventional radical polymerization conditions initiated with AIBN (sample 6). Polymers with low molar mass, $DP_n \sim 15-20$ (samples 1 and 2), moderate molar mass, $DP_n \sim 50$ (samples 3 and 4), and high molar mass, $DP_n \geq 100$ (samples 5 and 6), were prepared.

Figure 3 shows the most characteristic regions (CH and CH_2 groups of the polymer backbone) in the ^{13}C NMR (75 MHz) spectra of all samples. The results published in refs 38 and 39 were used to assign the signals. Tacticity as measured by integration of CH-based triads is approximately the same for all samples: *mm*/*mr*/*rr* = 0.18/0.47/0.35, which agrees with literature data[39] for anionic polymerization of *t*BA with BuLi. Thus, the tacticity of poly-*t*BA does not depend on the method of preparation (NMP, ATRP, conventional technique, or even anionic polymerization).

Figure 3 shows that the CH and CH_2 groups in the carbon spectrum of sample 1 have a slightly different pattern than the spectra of the other samples. This

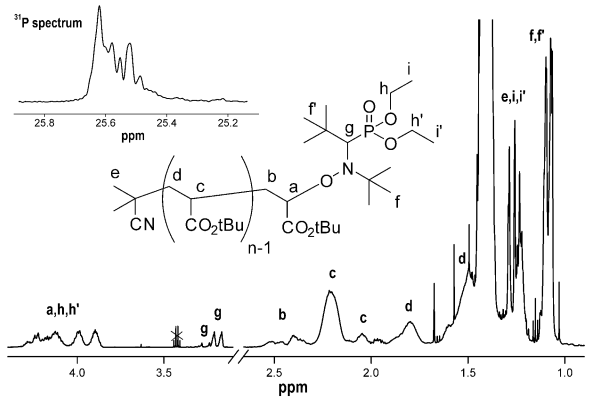


Figure 4. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of sample 1. Inset: ^{31}P NMR spectrum.

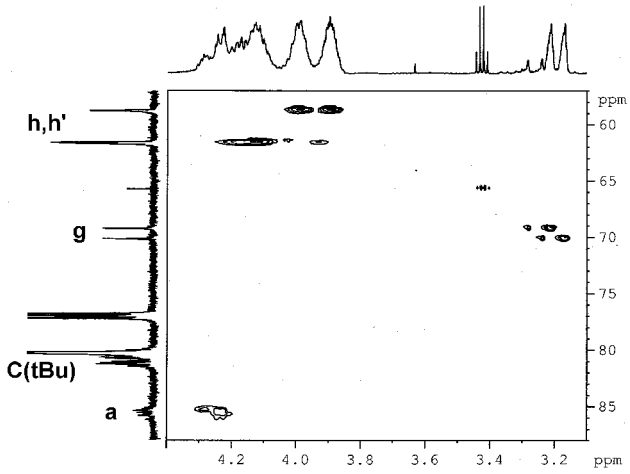


Figure 5. Fragment of ^{1}H−^{13}C−HSQC spectra (downfield region in ^{13}C) of the sample 1. See Figure 4 for structural assignments.

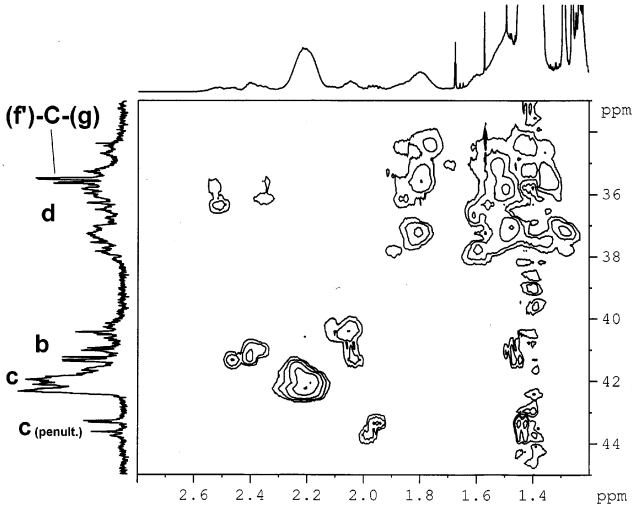


Figure 6. Fragment of ^{1}H−^{13}C−HSQC spectra (upfield region in ^{13}C) of sample 1. See Figure 4 for structural assignments.

could be due to slightly different chemical shifts from either the last, the penultimate, or even more distant units in the polymer chain. Since the chain length is short ($DP_n \sim 15$ unit), the signals for all units do not "equilibrate" into one broad signal. This permits analysis of the configuration of the end units in sample 1 by comparison with sample 2 since samples 1 and 2 have similar chain lengths but were prepared by different CRP methods (NMP vs ATRP).

Analysis of Short Chain Length Polymers by 600 MHz NMR. Samples 1 and 2 were analyzed by 2D NMR. According to GPC data, they both have relatively short chain lengths ($M_n = 2000-2300$, $DP_n = 14-18$). For such short chains, NMR becomes a powerful tool to precisely evaluate functionality and stereochemical configuration.

The ^{1}H NMR spectrum of sample 1 is shown in Figure 4, and the signals of CH−O group of the last unit and of CH_2 groups in the DEPN moiety are strongly overlapped (region around 4 ppm in Figure 4), although the CH−P doublets of the nitroxide end are resolved (3.2 ppm). These doublets look similar to the doublets seen in the spectra of the alkoxyamine (Figure 1). Integration of these signals and signals of CH group in the backbone provides an estimate of the molecular weight, which agrees with the averaged molecular weight of the polymer $M_n \sim 2200$ ($DP_n \sim 15$), assuming high chain end functionality. The integral ratio of the larger doublet to the smaller one in the spectrum is approximately 7:1. This ratio is larger than the ratio of isomeric *t*BP-DEPN alkoxyamines at equilibrium (5:1 in Figure 1). Therefore, we conclude that attachment of a polymer chain to *t*BP-DEPN alkoxyamines does not affect the diastereomeric ratio significantly.

Figures 5 and 6 show fragments of ^{1}H−^{13}C−HSQC spectra for sample 1 (downfield and upfield regions in ^{13}C NMR, respectively). The groups of interest are the CH in penultimate unit and the CH−O in the last unit. The CH−P group in the nitroxide could also confirm the diastereomeric ratio derived from the proton spectrum. However, the CH−P doublet (69.65 ppm, $^{1}J_{C-P} = 139$ Hz) was not split into different signals due to the presence of diastereomers, as was clearly observed in the ^{1}H spectrum (Figure 5, cross-peaks in the 70−3.2 ppm region). The different CH−O groups originating from different triad configurations (Figure 5, cross-peaks in the 85−4.3 ppm region) are not satisfactorily resolved in the ^{13}C NMR spectrum (Figure 5), too. However, CH signals of the penultimate unit are relatively well resolved (Figure 6, cross-peaks at 43.5−1.9 ppm) and were used for the analysis. The four signals at ca. 43.5 ppm were assigned to *mm*, $\delta = 43.74$; *mr* (or *rm*), $\delta = 43.61$; *rm* (or *mr*), $\delta = 43.31$; *rr*, $\delta = 43.26$. The *rm* and *mr* are not equivalent in the last triad.[40] The integral ratio $mm/mr + mm/rr = 0.18/0.48/0.34$ agrees very well with the averaged tacticity of the backbone. This result allows one to conclude that neither the stereoconfiguration of the penultimate units nor more remote units in the polymer chain are affected by the different stability of terminal alkoxyamines.

NMR analysis was also performed on sample 2, a polymer of similar molar mass but prepared by ATRP and, of course, without diastereometric effects originating from chiral end groups. Its ^{1}H NMR spectrum (600 MHz) is shown in Figure 7. The molecular weight of the polymer estimated from the end group, $M_n \sim 2900$ ($DP_n \sim 22$), is higher than that estimated from GPC using pMMA standards. Some loss of functionality could be due to higher radical concentrations in the ATRP system. The methine protons in the CH−Br end group are clearly observed in the ^{1}H NMR spectrum in the region 4.0−4.2 ppm. It is split into three groups of multiplets: "doublet-of-doublet" (*mm*) at $\delta = 4.13$, "doublet-of-triplet" (*mr*) at $\delta = 4.07$, and "triplet" (*rr*) at $\delta = 4.03$. These multiplets unambiguously reflect the tacticity of the last triad in the polymer backbone, which

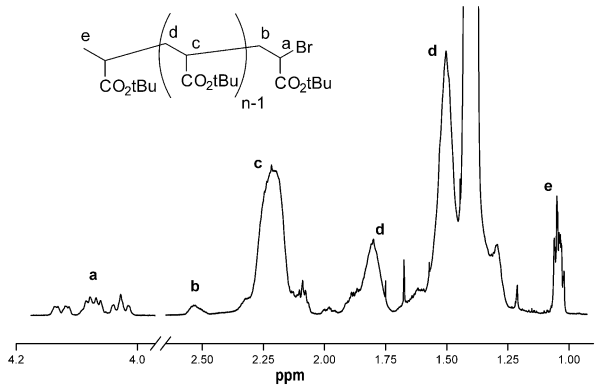


Figure 7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of sample 2.

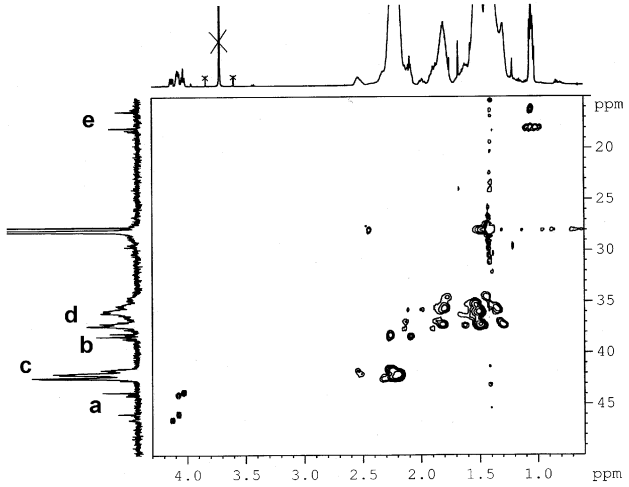


Figure 8. ^{1}H−^{13}C−HSQC spectrum of sample 2. See Figure 7 for structural assignments.

is *mm*/*mr*/*rr* = 0.22/0.45/0.33, similar to the averaged tacticity of the backbone taking into account accuracy of integration. The same ratio is calculated from the ^{13}C NMR spectrum (Figure 8, cross-peaks in the 45−4.0 ppm region). The carbon signals in this range can be assigned as *mm*, δ = 46.5; *mr*, δ = 45.93; *rm*, group of signals at δ = 44.15−43.98; *rr*, δ = 43.81.

Conclusion

Although a large ratio of diastereomers can be found in the monomeric alkoxyamine *t*BP-DEPN (∼5:1) and also in the terminal group of polymeric alkoxyamines (∼7:1), there is no control over tacticity in the polymerization of *tert*-butyl acrylate using the monomeric alkoxyamine *t*BP-DEPN as a polymerization mediator. The triad distribution in the main chain of poly(*tert*-butyl acrylate) prepared in the presence of chiral nitroxides, in an ATRP process, and by conventional polymerization is essentially the same. Even the last triad seems to follow the distribution observed in free radical polymerization, despite the neighboring chiral group.

The diastereomeric ratio originates predominantly from stereoselective decomposition rather than through the coupling process. However, regardless of the origin of stereoselectivity, the generated radical is sp^2-hybridized and must exist for a relatively long time in the reaction media before adding to monomer (k_p ∼10^4 M^{-1} s^{-1}).[41] Using the average lifetimes of various species at different states,[42] one can calculate that, in bulk *t*BA, after a radical is generated it will react with monomer only after $t = 1/(k_p[M])$, i.e., ∼10^{-5} s. The same radical can react with DEPN ([DEPN] = 0.001 M, k_c ∼10^8 M^{-1} s^{-1})[37] after $t = 1/(k_c[DEPN])$, i.e., also ∼10^{-5} s. However, the lifetime in a solvent cage, when the radical is still in the chiral environment induced by the DEPN, is only ∼10^{-9} s. Thus, the radical rapidly "forgets" how it was generated. There are thousands of collisions of the generated radical with monomer, solvent, and DEPN molecules before propagation happens. The deactivation reaction of the growing chain with DEPN will occur after one of a few monomer additions under these conditions. Therefore, although the last unit of the dormant chain may be in one strongly preferred configuration, its contribution to chain growth is negligible, and its contribution to the overall tacticity diminishes with chain length. Therefore, it may be more promising to incorporate permanent or temporary (e.g., via complexing Lewis acids or solvents) auxiliary groups, using either template polymerization or conducting polymerization in a confined space or with inclusion complexes, if one wishes to control polymer tacticity in radical polymerizations.

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