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Notes

Alternating Free-Radical Isomerization Polymerization of Methyl α-Isobutylacrylate

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Introduction

We recently described the synthesis of poly(methyl α-alkylacrylates) containing alkyl pendant groups of variable size and branching.[1] The well-known difficulty in polymerizing α-alkylacrylate monomers when the alkyl substituent is larger than a methyl (MMA) was overcome by using high pressures as both a kinetic and thermodynamic additional driving force for the free-radical polymerization. This methodology allowed us to obtain for the first time acrylic polymers that are thermodynamically unstable at room temperature and pressure (ceiling temperature T_c < 25 °C) and whose metastability could be used to generate lithographic pattern by controlled degradation in the presence of external triggers (heat, UV light, e-beam).[2] An ongoing investigation of the structure−degradability relationships in this series of polymers indicated a very peculiar behavior for one of the polymers, poly(methyl α-isobutyl acrylate), that could not be rationalized easily and forced us to reconsider its assigned structure **A**. In this note, we will present a full NMR reinvestigation of the polymer and describe a previously unreported, efficient intramolecular rearrangement of the acrylic propagating free radicals whose thermodynamic driving force largely derives from the need to minimize steric strain in these highly crowded polymers.

Experimental Section

Synthesis of the monomer, methyl α-isobutylacrylate (M*i*BA), and its high-pressure free-radical polymerization were conducted as previously reported.[1] A typical example is as follows: 1.43 g of M*i*BA (1.0 × 10^{-2} mol) carefully deoxygenated with nitrogen for 20 min and 0.011 g of 2,2′-azobis(isobutyronitrile) (6.7 × 10^{-5} mol) were mixed and transferred under a nitrogen atmosphere to a 1.3 mL Teflon reaction vessel until the container was fully loaded. The ampule was hermetically closed and weighed to calculate the exact amount of monomer and initiator. The polymerization was run at 5 kbar and 65 °C for 6 h, using a high-pressure reactor designed by the High-Pressure Research Center of the Polish Academy of Science. Precipitation in hexanes yielded 0.102 g of a white powder (13.4%), with the following molecular weight characteristics as determined by SEC (THF, poly(methyl methacrylate) calibration): $M_n = 40 \times 10^3$, $M_w/M_n = 1.61$. Thermogravimetric analysis (DuPont TA 2050, 10 K min^{-1}, nitrogen) of the obtained poly(methyl α-isobutylacrylate) showed that no decomposition leading to volatile products took place below 190 °C (full thermogram provided as Supporting Information).

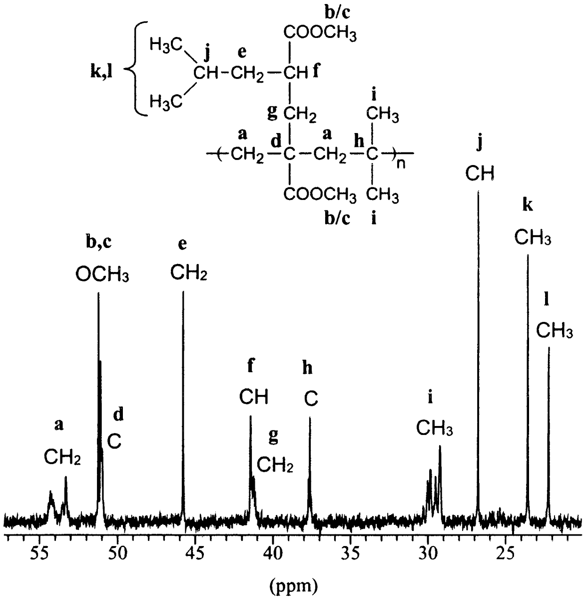

Figure 1. ^{13}C NMR spectrum of poly(M*i*BA).

NMR spectra were recorded at 150 °C in d_5-nitrobenzene using a Bruker Avance 600 spectrometer operating at 600.03 MHz (^1H) and 150.88 MHz (^{13}C). For ^1H NMR analysis, samples with a concentration of 10 mg mL^{-1} were used, and chemical shifts were referenced to the most upfield solvent resonance of nitrobenzene at 7.50 ppm. ^{13}C NMR spectra were recorded under proton decoupling at a concentration of 100 mg mL^{-1} and the most upfield peak of the solvent resonance at 123.5 ppm. Conditions for the ^{13}C NMR experiments were not optimized to allow quantitative analysis. A DEPT technique was used to determine multiplicity of the peaks in the ^{13}C spectra. 2D NMR experiments, phase-sensitive $^1H-^1H$ COSY and $^1H-^{13}C$ HETCOR, were used to establish couplings between corresponding nuclei. Proton−carbon correlation was performed with direct carbon observation because of the absence of a gradient probe that would take the requisite high temperature. The delay before the final 90° antiphase refocusing pulses was 3.45 ms followed by a 2.29 ms delay to capture intensity from all carbon multiplicities. Forty two 32-scan, 4K slices were obtained with 0.3 s acquisition time and 2 s recycle delay. TPPI phase-sensitive proton−proton COSY spectra were obtained from 128 4-scan 2K slices with an 0.426 s acquisition time and 1 s recycle delay.

Results and Discussion

High-pressure (5−8 kbar) free-radical polymerizations of methyl α-isobutylacrylate initiated by 2,2′-azobis(isobutyronitrile) at 65 °C resulted in a white, powdery polymer soluble in most common organic solvents. The ^{13}C NMR spectrum of the polymer is shown in Figure 1, with the degree of substitution for each carbon (C, CH, CH_2, CH_3) as determined by DEPT indicated for each peak (see Supporting Information for the full spectra). The ^1H NMR spectrum of the polymer is presented in Figure 2, with the proton peaks unambigu-

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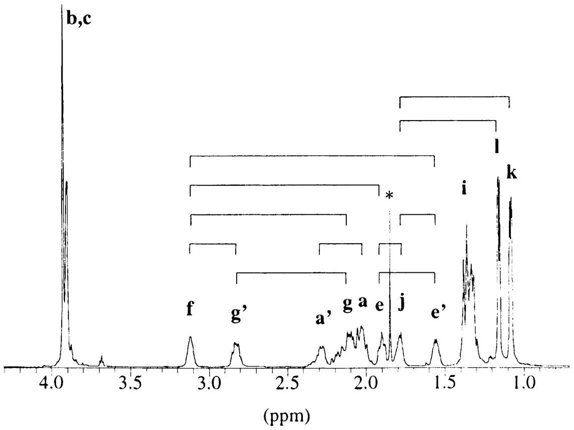
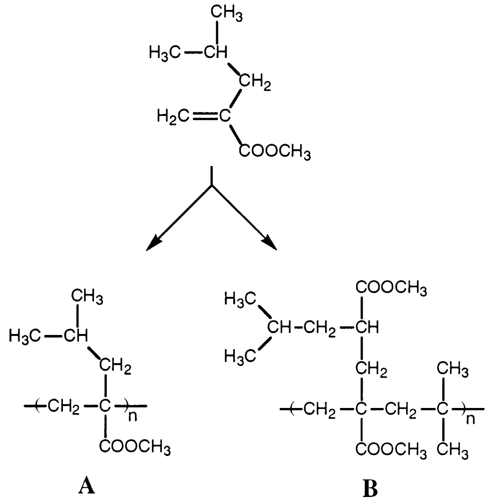


Figure 2. ^{1}H NMR spectrum of poly(M*i*BA). Brackets indicate the couplings between protons as determined by a ^{1}H−^{1}H COSY experiment.

Scheme 1



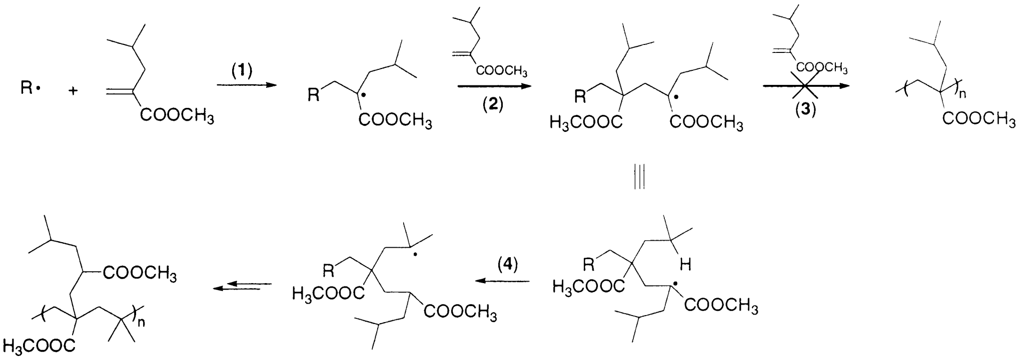
ously assigned by a ^{1}H−^{13}C HETCOR experiment (Supporting Information). Couplings between protons as determined by ^{1}H−^{1}H COSY (Supporting Information) are also indicated in Figure 2.

Assuming that the polymerization proceeds through a vinyl double bond addition in a traditional way, structure **A** should be obtained for the polymer. In the ^{13}C NMR spectrum, peaks expected for structure **A** are observed (methyl groups **k** and **l**, methine group **j** from the isobutyl side group) together with another set of peaks shifted downfield, suggesting the existence of an isomeric structure. Particularly noticeable are two tertiary (**f** and **j**) carbons separated by more than 10 ppm. The observed difference in chemical shifts for the two sets of peaks cannot be explained simply by the presence of stereoisomeric units as tacticity usually leads to small variation in chemical shifts, typically within a few ppm range. Likewise, in the ^{1}H NMR spectrum, two methine protons separated by more than 1 ppm can be observed, with one of the peaks showing up above 3 ppm, a highly unusual chemical shift for a simple aliphatic CH.

Clear evidence that structure **A** is wrong arises from the ^{1}H−^{1}H COSY experiment, the results of which are summarized in Figure 2. The two most striking features are (a) one of the methyl groups **i** is not coupled to any of the CH's and (b) one of the CH protons **f** is coupled to the protons of two different CH_2 groups. To account for this spectroscopic evidence, structure **B** has to be assumed for the polymer. This isomeric structure can be obtained as a result of an intramolecular hydrogen transfer process during propagation (Scheme 2). Assignment of carbons for structure **B** is shown in Figure 1. Methyl groups **l** and **k** are part of the isobutyl side group and are in slightly different electronic environments probably due to some hindered rotation around the $C_{\mathbf{j}}-C_{\mathbf{e}}$ bond. Methyl groups **i** are directly attached to the backbone, and their ^{1}H and ^{13}C NMR signals show multiple splittings, which can be attributed to a stereoisomeric effect (tacticity with respect to the substituents on the carbon **d**). In the proposed structure **B**, methyl protons **i** cannot be coupled to any other proton as they are attached to a quaternary carbon. The methine proton **j** of the isobutyl side group is coupled to protons of both methyl groups **l** and **k** ($J = 6.3$ Hz) as well as to the methylene protons **e**, as expected. The methine group **f**, which is formed during the intramolecular 1,5 hydrogen shift, is similar to the CH groups of a polyacrylate backbone. In agreement with this fact, its ^{1}H (3.1 ppm) and^{13}C (41.5 ppm) chemical shifts are very close to the values observed for polyacrylate methine groups (2.4−2.8 and 41−42 ppm for ^{1}H and ^{13}C, respectively).[3] Protons **f** are coupled to protons of two methylene groups **g** and **e**, a feature impossible to rationalize in terms of structure **A**. By integrating the ^{1}H NMR spectrum, it was possible to obtain the relative amounts of each proton in the polymer structure. From the 1:1 ratio of signals for protons **f** and **j** and 1:6 ratio for protons **f** and **b** + **c**, it is possible to conclude that structure **B** effectively describes the polymer, with no structure **A** present as a comonomer unit.

Intramolecular 1,5-hydrogen shifts are facilitated by the formation of a six-membered ring transition state and have been widely observed for small free radicals.[4] A few examples of such shifts are also known in polymer

Scheme 2



chemistry, the most common example being the free-radical polymerization of ethylene to branched low-density polyethylene.[5] Intramolecular hydrogen shifts in this backbiting mode have also been reported to occur to some extent during the free-radical polymerizations of acrylates.[6−8] The rearrangement reported here is unique in the fact that the alkyl radical resulting from the rearrangement is thermodynamically less stable than the initial ester group-stabilized, propagating free radical. It seems reasonable to assume that in this case the thermodynamic driving force arises in part from the release of the steric strain in the polymer that results from the intramolecular hydrogen shift.

Another noteworthy feature of this rearrangement results from the fact that the 1,5-hydrogen shift (step 4 in Scheme 2) occurs much faster than the propagation (step 3). As a result, a clean alternating structure **B** is obtained, with side-to-side insertion of two two-carbon units: an isobutylene and a complex, α-branched methyl acrylate.

A few isomerization polymerizations have been described in the literature where the propagating species rearrange rapidly by either a ring-opening or a proton or hydride shift, before addition of the resulting species to another monomer molecule occurs.[9−11] To the best of our knowledge, all of these isomerizations involve atoms that are part of the last added unit. In the case investigated here, isomerization requires the subsequent addition of two units, the rearrangement taking place only after the second unit has been added and involving a hydrogen shift from the first to the second unit.

The unexpected rearrangement described in this note provides another striking example of the difficulty associated with the polymerization of olefins 1,1-disubstituted by large substituents. The steric strain associated with the presence of bulky substituents on every second carbon alongside the backbone makes polymerization of these monomers very difficult. The use of high pressures allows to partly circumvent the problem, but it must be realized that under these more extreme conditions reactions unreported under "normal" conditions can appear, entirely modifying the expected course of the polymerization.

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Supporting Information Available: ^{13}C NMR, DEPT, ^{1}H NMR, ^{1}H−^{1}H COSY, and ^{1}H−^{13}C HETCOR spectra and TGA thermogram of the polymer. This material is available free of charge via the Internet at http://pubs.acs.org.

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