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Carbocationic polymerization in suprecritical CO_2

III. The ceiling temperature of and the effect of temperature on the polymerization of isobutylene

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Abstract

The polymerization of isobutylene (IB) in supercritical carbon dioxide (SC·CO_2) has been investigated in the temperature range from 32.5 to 47.5 °C at 139±3 bar. The ln M_n of polyisobutylene (PIB) versus 1/T plot gave $\Delta H^{\ddagger}_{Mn,PIB}$=-14.1±1.5 kcal/mol (-59.1±6.3 kJoule/mol) and $\Delta S^{\ddagger}_{Mn,PIB}$=-31.1±6.2 cal/mol·deg (-130.2±26.0 Joule/mol·deg). These quantities are quite different from those obtained in conventional liquid systems. The ceiling temperature (T_{ceil}) was determined by linear extrapolation of the ln M_n versus 1/T plot to the molecular weight of the monomer. According to this procedure the T_{ceil} of IB polymerization in SC·CO_2 in about one molar solution at 139±3 bar is 88±9 °C.

Introduction

In the course of our investigations concerning the polymerization of IB in SC·CO_2 we found that well-defined ^{t}Bu-PIB-Cl^t can be synthesized in SC·CO_2 by using $TiCl_4/BCl_3$ mixtures in conjunction with 2-chloro-2,4,4-trimethyl-pentane (TMPCl) at 32.5 °C [1]. During our experimentation we have consistently observed that at this temperature level the monomer conversion and number average molecular weight (M_n) reach an upper limit of ~45% and ~2000 g/mol, respectively [1,2]. Above this temperature undesirable side reactions (e.g. HCl loss) started to occur and precisely-defined products could not be obtained.

For most chain polymerizations there is a temperature at which the reaction becomes reversible, that is the rate of polymerization (propagation) becomes equal to that of depolymerization (depropagation) [3]. Above this temperature, the so called T_{ceil}, the rate of depolymerization is greater than that of propagation, and polymerization will not proceed. The T_{ceil} is affected by monomer concentration and pressure [3,4].

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Surprisingly, reliable information is unavailable regarding the T_{ceil} of IB polymerization. Dainton and Ivin [5] collected thermodynamic data on the polymerization of select monomers. They determined $\Delta H°$ (-12.8 kcal/mol) and calculated $\Delta S°$ (-37 cal/mol·deg) for IB polymerization, and by use of these values Wall estimated $T_{ceil,PIB}$ to be 50 °C [6].

Czechoslovak authors [7] carried out IB polymerization in the -50 °C to +21 °C range and estimated $T_{ceil,PIB}$~120 °C from the viscosity average molecular weight (M_V) versus reciprocal temperature (Arrhenius) plot.

Japanese authors [8] polymerized IB in the gas phase. Above 50 °C the polymerization did not proceed although the formation of a "small amount of nonviscous liquid product" was observed. Their results indicated the existence of a $T_{ceil,PIB}$ between 50 and 100 °C.

Against this background, we decided to study the effect of temperature on IB conversion, PIB molecular weight, and PIB chain-end structure, and to determine the T_{ceil} of IB polymerization in SC·CO_2.

Experimental

The synthesis and purification of TMPCl and the source of IB, BCl_3, $TiCl_4$ and CH_3Cl (MeCl) have been published [9-11].

The experiments were conducted by using a Hastelloy C pressure reactor. Details of the equipment have been described [2]. The syntheses were carried out with $TiCl_4/BCl_3$ mixtures as described in ref. [1] and with the use of the reagent concentration shown in the legend of Table 1. Details of NMR and GPC analyses have been published [11,12].

Table 1. Polymerization of IB in Supercritical CO_2: The Effect of Temperature on Conversion, M_n, and Chain-End Structure

(Conditions: [TMPCl]=0.012 mol/L, [$TiCl_4$]=0.122 mol/L, [BCl_3]=0.085 mol/L, [IB]=1.215 mol/L, 5 vol.% MeCl, Vol.=300 mL, P=139±3 bar)

				Chain-end structure	
T	Conv.	M_n	M_w/M_n	C=C	-Cl^t
°C	%	g/mol		mol%	mol%
32.5	40	2000	1.4	not detectable	>99
37.5	19	1471	1.8	40 (endo & exo)	60
42.5	7	875	multi modal	52 (endo & exo)	48
47.5	4	710	multi modal	56 (endo & exo)	44
88*	-	56	0	0	0

* by linear extrapolation of the Arrhenius plot (see Figure 2)

Results and Discussion

We investigated the effect of temperature in the range of 32.5 to 47.5 °C on IB conversion, PIB molecular weight and chain-end structure. Table 1 shows reaction conditions and results. Both the conversion and molecular weights show a marked decrease with increasing temperatures.

Figure 1 shows the effect of temperature on IB conversion. Monomer conversion sharply decreases with increasing temperature and extrapolation of the fitted curve suggests that the T_{ceil} is above 60 °C.

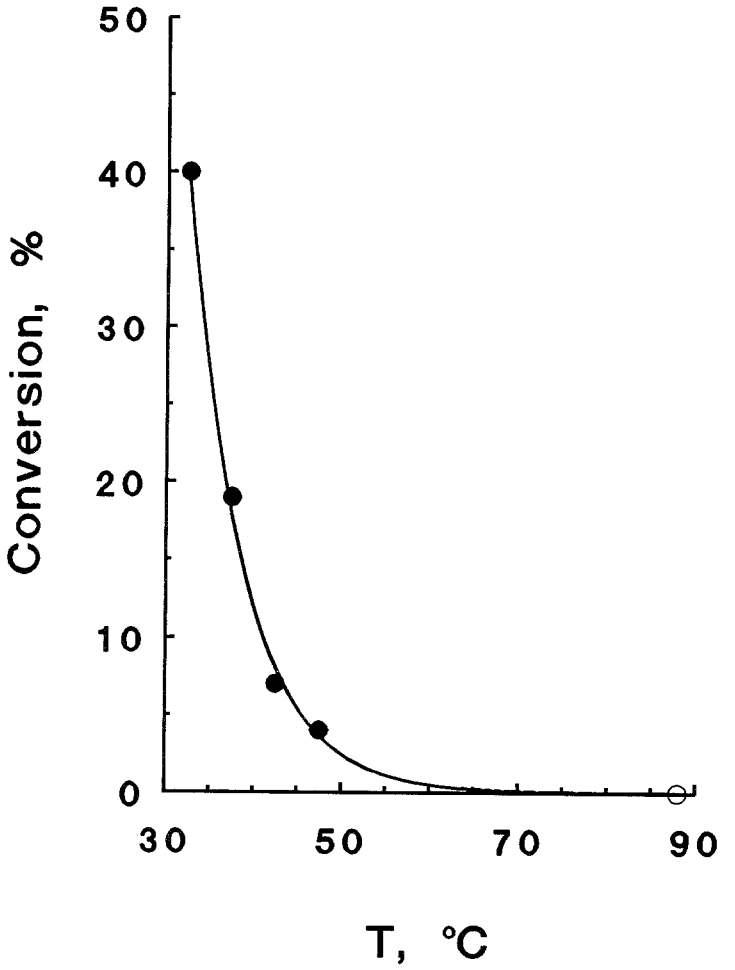


Figure 1. The Effect of Temperature on the Conversion of IB Polymerization in SC·CO_2 (Conditions in Table 1; Solid dots measured, empty circle calculated.)

Figure 2 depicts the effect of temperature in the 32.5-47.5 °C range on PIB molecular weights. According this Arrhenius plot $\Delta H^{\ddagger}_{Mn,PIB}$=-14.1±1.5 kcal/mol (-59.1±6.3 kJoule/mol) and $\Delta S^{\ddagger}_{Mn,PIB}$=-31.1±6.2 cal/mol·deg (-130.2±26.0 Joule/mol·deg). These quantities are quite different from those obtained in conventional liquid systems [13]. The high $\Delta H^{\ddagger}_{Mn,PIB}$ value suggests that the growing species are ion pairs and that the molecular weight controlling event is chain transfer to monomer [13]. The low $\Delta S^{\ddagger}_{Mn,PIB}$ indicates that molecular weights are determined by enthalpy [13].

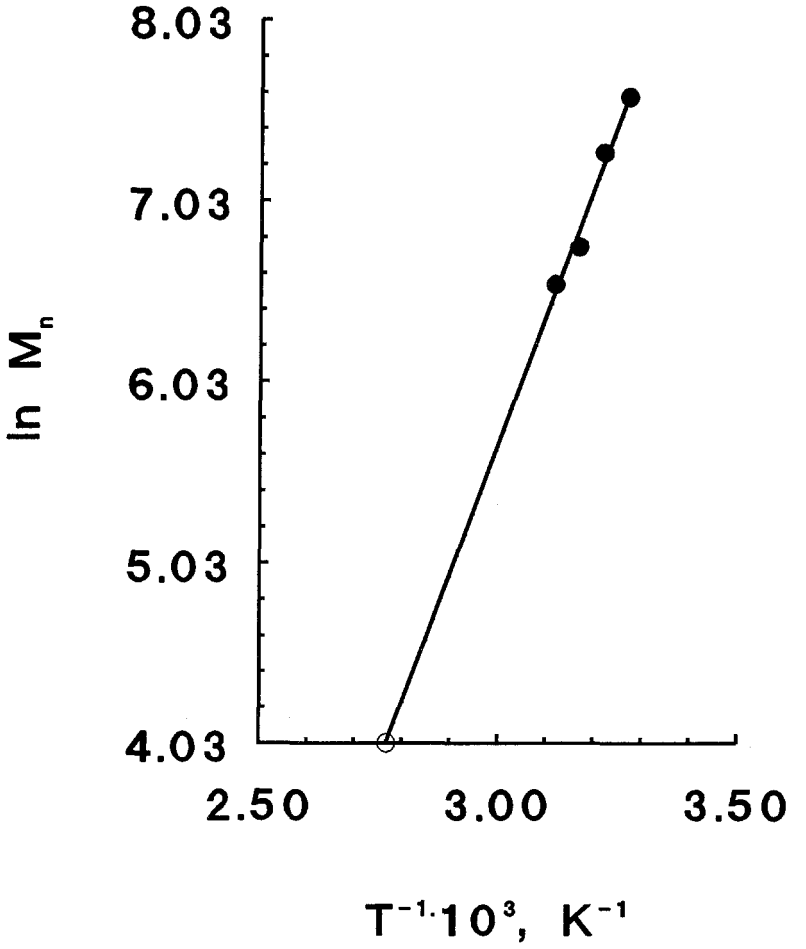
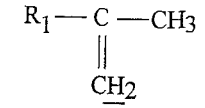
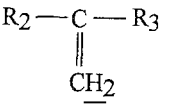


Figure 2. The Effect of Temperature on the M_n of PIB obtained in SC·CO_2 (Conditions as in Table 1)

The T_{ceil} of IB polymerization in SC·CO_2 was determined from Figure 2 by linear extrapolation of the molecular weight data to M_n=56 (ln 56 = 4.03), the molecular weight of IB. According to this procedure T_{ceil} = 88±9 °C, a value similar to that suggested for conventional liquid systems [3,5-8].



1



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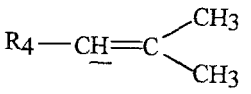

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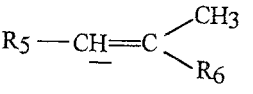

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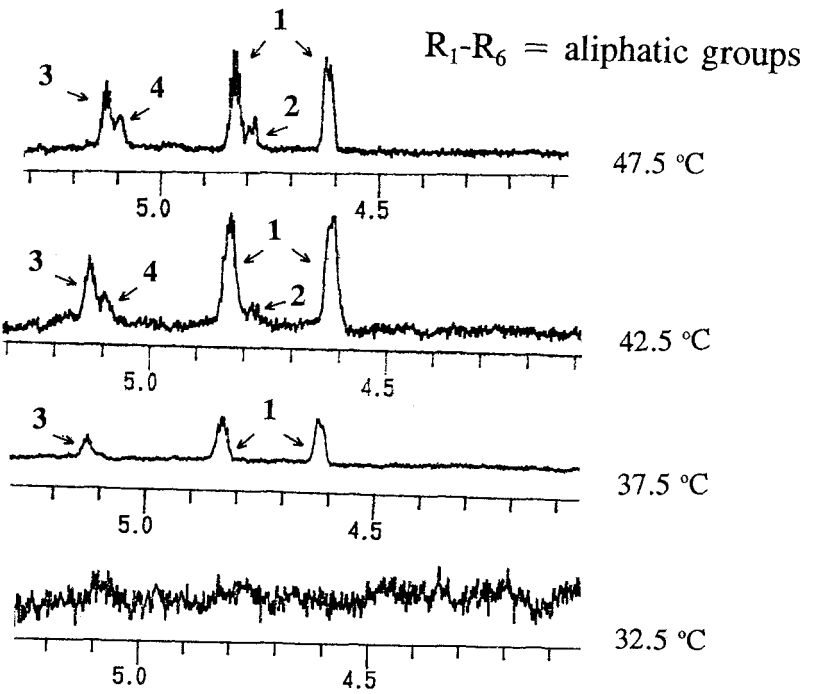

Figure 3. ^{1}H-NMR Spectra of the Olefinic region of the PIB at Different Temperatures (Conditions as in Table 1).

While the precision of our extrapolation method is at best moderate, it still yields a reasonably acceptable T_{ceil} (reflected by the ±10% error limits), because the extrapolation occurred only over ~40 °C. In contrast, extrapolation to estimate T_{ceil} by the use of molecular weight data obtained under conventional liquid conditions [13] leads to unreliable values because the extrapolation has to be done over a much wider temperature interval (~100 °C).

Figure 3 shows the olefinic region of ^{1}H-NMR spectra of PIBs obtained at 32.5, 37.5, 42.5 and 47.5 °C. The doublet (indicated by 1) at 4.61 and 4.82 ppm is characteristic of CH_2= protons of the external terminal double bond. The singlet (indicated by 3) at 5.12 ppm is due to the -CH= proton of the internal terminal double bond. These terminal double bonds [1,3] indicate deprotonation (i.e., chain transfer) during polymerization. The non-terminal double bonds (indicated by 2 and 4) may arise because of various isomerization/ deprotonation reactions at an elevated temperature [1,12,14]. Gratifyingly, the product harvested at 32.5 °C does not indicate the presence of any double bonds (i.e., chain transfer during polymerization) and, therefore, shows that the synthesis of well-defined ^{t}Bu-PIB-Cl^t is quite feasible at a surprisingly high temperature [1].

Acknowledgement

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