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14. ABSTRACT

Lithium cation catalyzed radical copolymerization of isobutylene with ethyl acrylate has been examined. Up to 30% of isobutylene is incorporated at 1 atm pressure, and molecular weights up to a million have been observed.

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Polar-Nonpolar Radical Copolymerization under Li+ Catalysis

ABSTRACT

Lithium cation catalyzed radical copolymerization of isobutylene with ethyl acrylate has been examined. Up to 30% of isobutylene is incorporated at 1 atm pressure, and molecular weights up to a million have been observed.

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Graduate Students	
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Jan Budin	1.00
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Total Number:	**1**

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Douglas Caskey	1.00
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Polar-Nonpolar Radical Copolymerization under Li⁺ Catalysis
FINAL REPORT
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Contract: W911NF-07-1-0221

TABLE OF CONTENTS

Introduction. Our initial focus is the Li^+ catalyzed radical copolymerization of isobutylene (IB) with ethyl acrylate (EA). The rationale for this choice is given in the proposal. Our objective is an optimization of polymerization conditions and control of polymer composition (% of IB and % EA), and molecular weight (M_w). We also wish to know the polymer molecular weight distribution (MWD), structure (branching, random vs. block or alternating structure) and the polymerization mechanism. For all this, we needed to develop separation and analytical characterization methods. The molecular weights given in this report are only qualitative due to instrumental limitations. Our GPC instrument is old and is equipped with a refractive index detector only. We use calibration with ordinary (linear) polystyrene standards although our homopolymer samples are certainly highly branched and our copolymers probably are as well. To remedy the situation, we have submitted a proposal to the DURIP program requesting a modern GPC instrument that also has light-scattering and viscosimeter detectors. This would permit us to obtain true molecular weights. We have been fortunate in finding an industrial partner (BASF) sufficiently interested in our work to run HPLC on our samples.

Ultimately, we will need to optimize the structure of the lithium carborane catalyst, but for the time being we use $LiCB_{11}Me_{12}$, which is the easiest to prepare.

Homopolymerization.   The study of this copolymerization process requires an understanding of the radical homopolymerizations of the two comonomers. While the radical polymerization of EA is well described in the literature, the radical polymerization of IB is normally not possible and is only enabled by Li^+ catalysis. The relevant results obtained in our laboratory have not yet appeared in the literature and are just being submitted this week. They will be briefly summarized here, and then we will turn to the description of our copolymerization results.

The polyisobutylene (*b*-PIB) that is produced by homopolymerization of IB in an inert solvent such as 1,2-dichloroethane or toluene, catalyzed with $LiCB_{11}Me_{12}$ and initiated with a non-oxidizing radical source, is highly branched and entirely different from the linear polyisobutylene (*l*-PIB) produced under the usual cationic initiation. The difference is clear in spectral (NMR) and physical (DSC, TGA, HPLC) properties. A detailed 2D-NMR examination of *b*-PIB obtained from ordinary IB and several isotopically labeled versions of IB revealed that its backbone is very highly branched and the branches are linear PIB segments terminated with isobutyl groups and containing five IB units on the average (the average value is lower than five if the main chain is not fully branched and contains linear segments as well). The main chain is terminated with a substituent derived from the initiating radical on one end, and with the $CH_2=C(Me)CH_2-$ group on the other end.

Selected examples of results from polymerization runs are presented in Table 1. They were obtained under non-oxidizing conditions of initiation, photochemical decomposition of azo-*t*-butane (ATB), which produces *t*-butyl radicals, or di-*t*-butyl peroxide (DTBP), which produces *t*-butoxy radicals. IB was used in excess at 1 atm pressure and the reaction was allowed to proceed for 24 h, which is long enough that all initiator was decomposed. The concentrations of the catalyst and the initiator were 10% by weight. The reactions were run on small scale (0.5 mL of solvent). As is apparent in Table 1, under these conditions only *b*-PIB is formed.

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Table 1. Results of Selected IB Homopolymerization Runs under Non-Oxidizing Conditions

run	Initiator	solvent	PIB, mg	Type of polymer	M_w	MWD
1	DTPB	DCE	80	branched	1600	1.9
2	DTPB	toluene	200	branched	2800	2.0
3	ATB	toluene	210	branched	2200	1.8
4	ATB	DCE	22	branched	680	1.2

The best current mechanistic explanation for the formation of *b*-PIB is presented in Figure 1. We propose that the radical propagation step is accelerated considerably upon complexation of IB to the $LiCB_{11}Me_{12}$ catalyst, and competes successfully with the allylic abstraction that normally causes chain termination. To account for branch formation, we propose a backbiting H atom abstraction by the propagating radical after the addition of a few IB units. This H transfer is reversible and produces a quasi equilibrium between the more stable tertiary propagating radical and a less stable resulting secondary radical, in which the former dominates. In an EPR spectrum taken under conditions of steady irradiation (experiment kindly performed by Prof. Malcolm Forbes at Univ. of North Carolina), the tertiary propagating radical is clearly observed along with the initiating *t*-butyl radical, but the secondary radical resulting from the backbiting is not seen. To account for the product structure, we postulate that the reactivity of the secondary radical toward IB addition exceeds that of the tertiary radical to such a degree that it dominates further reaction and a branch results most of the time. The structure of the chain end group is accounted for if we postulate that the abstraction of a hydrogen atom from the end of the propagating radical is somewhat competitive with the addition of the next unit of IB after the backbiting step.
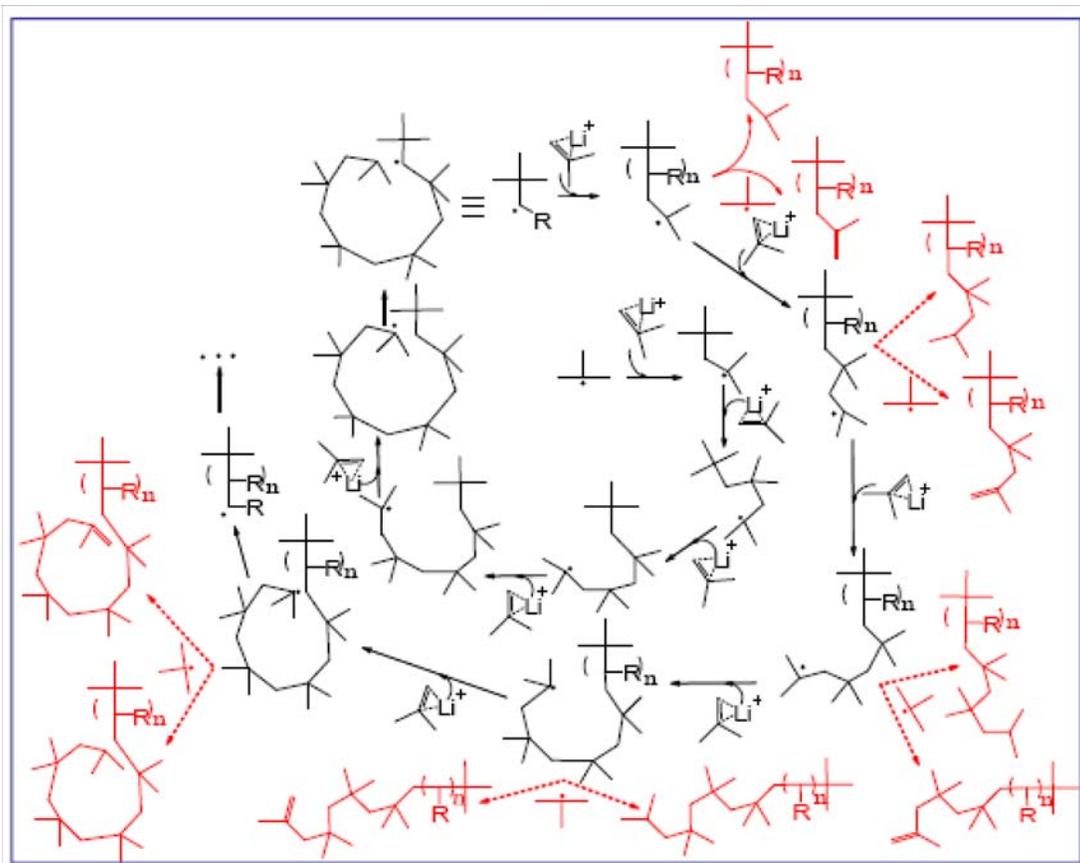
**Figure 1**. The best current mechanism for the formation of *b*-PIB

Under oxidizing conditions of initiation, we observe the formation of a mixture of *b*-PIB and *l*-PIB. The molecular weight of the former is lower, typically a few thousand, up to about 12 000. The molecular weight of the latter is higher, typically a few tens of thousands, up to 50 000. These polymers differ in solubility in hexane and can be easily separated. The ratio in which they are formed depends on reaction conditions. The formation of *b*-PIB can be suppressed with agents known to suppress radical polymerization and the formation of *l*-PIB can be suppressed with agents known to suppress cationic polymerization. We conclude that under oxidizing conditions a radical and a cationic polymerization chain are initiated concurrently and the two types of polymerization lead to distinct products. What is the initiation mechanism?

It is known from earlier studies that the $CB_{11}Me_{12}^-$ anion of the catalyst can be reversibly oxidized to the stable and isolable neutral radical $CB_{11}Me_{12}^{\bullet}$ at a potential about 1.15 V above ferrocene/ferricimium. It is reasonable to postulate that such oxidation proceeds slowly in the presence of an oxidizing agent such as atmospheric O_2 at room temperature or DTBP at elevated temperatures, and that the resulting $CB_{11}Me_{12}^{\bullet}$ radical acts as an initiator . This hypothesis is supported by the observation that pre-formed $CB_{11}Me_{12}^{\bullet}$ alone acts as a very effective initiator.

The $CB_{11}Me_{12}^{\bullet}$ radical is known to exhibit two types of reactivity. It is a one-electron oxidant and it is a methyl radical transfer agent. When it donates a methyl radical to a reaction partner such as a hexaalkyldisilane, a neutral species $CB_{11}Me_{11}$ is left behind. This is a carborane with a naked vertex, which has been isolated as a solid powder stable only at low temperature. It has been shown to act as an extremely strong Lewis acid, which attacks all sorts of nucleophiles that carry lone pairs (e.g., H_2O), but also nucleophiles carrying multiple bonds or aromatic rings. Thus, we propose that a transfer of a methyl radical from $CB_{11}Me_{12}^{\bullet}$ to IB triggers a radical polymerization chain that yields b-PIB and the resulting $CB_{11}Me_{11}$ byproduct concurrently triggers a cationic polymerization chain that yields l-PIB terminated with a carborate anion group (Figure 2). In support of the proposed mechanism, in the absence of the $LiCB_{11}Me_{12}$ catalyst, the $CB_{11}Me_{12}^{\bullet}$ radical triggers only a cationic polymerization of IB with the exclusive formation of l-PIB. The Li^+ catalyst is not needed for the cationic polymerization, only for the radical polymerization. Support for this mechanistic proposal has been obtained from the detection of the carborate anion substituent at the l-PIB chain end and by the use of the $CB_{11}(CD_3)_{12}^{\bullet}$ radical as the initiator. In this case, the CD_3 group is detected at the chain end of b-PIB and the five-fold symmetric $12\text{-}CB_{11}(CD_3)_{11}\text{-}$ group is detected at the chain end of the l-PIB product.
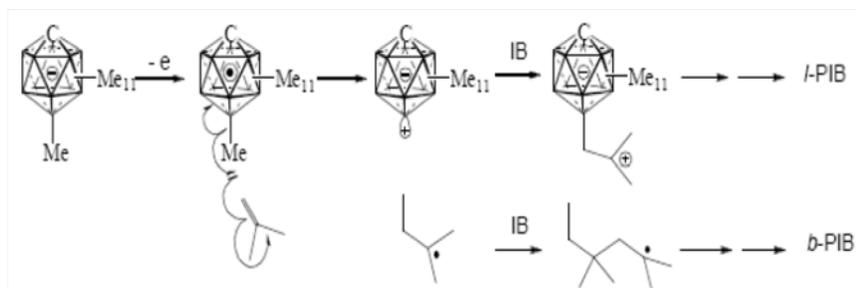

Figure 2. The proposed concurrent initiation of the formation of b-PIB by a radical mechanism and of l-PIB by a cationic mechanism in $CB_{11}Me_{12}^{\bullet}$ initiated polymerization of IB in the presence of $LiCB_{11}Me_{12}$ catalyst
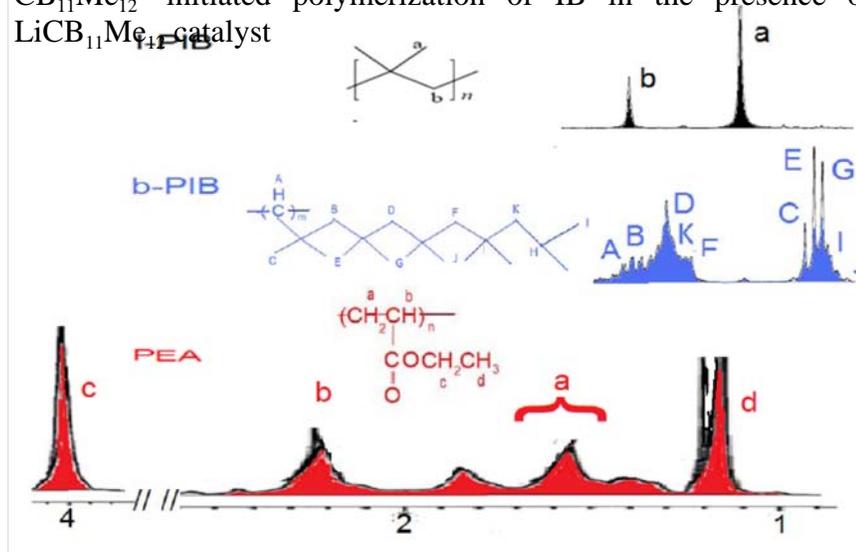
**Figure 3**. ^1H NMR spectra of l-PIB, b-PIB, and PEA.

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For the purpose of comparison, we show in Figure 3 the NMR spectra of the homopolymers *l*-PIB, *b*-PIB, and PEA.

Copolymerization. An alternating radical copolymer of IB with EA has been prepared by our industrial partner, BASF, under catalysis with $EtAlCl_2$ in toluene, following a 1995 Japanese publication. It serves as a standard for comparison with our results and its ^{1}H NMR spectrum is shown in Figure 4. The HPLC trace of this product is shown in Figure 5.
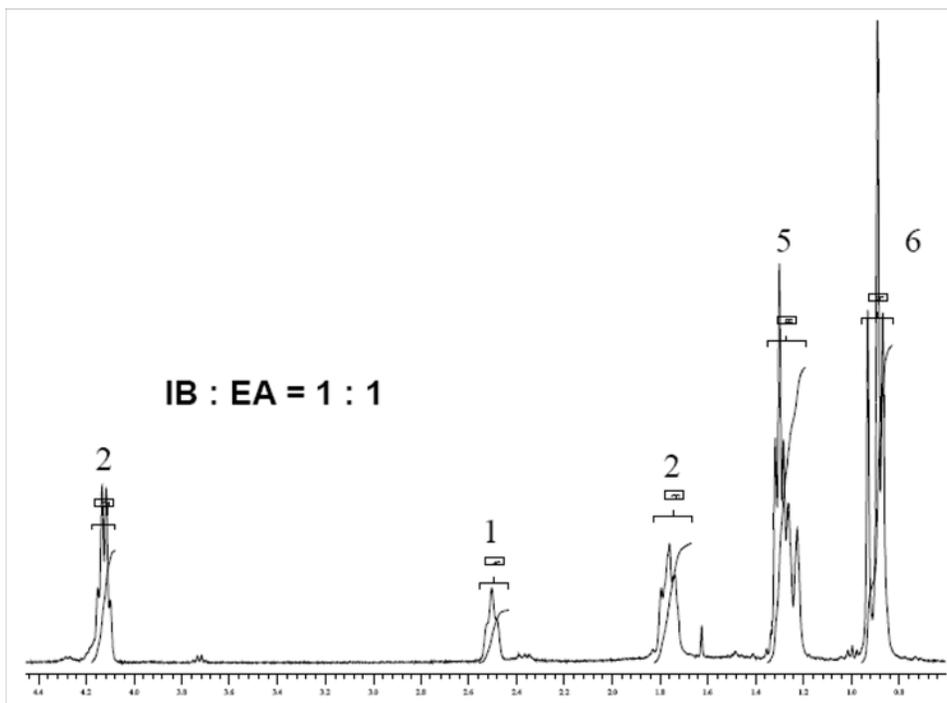
Figure 4. ^{1}H NMR spectrum of a 1:1 alternating copolymer of IB and EA obtained by BASF (see text). Integrals are indicated.

We have run a series of IB-EA copolymerization reactions with the $LiCB_{11}Me_{12}$ catalyst under the following general conditions: The $LiCB_{11}Me_{12}$ catalyst (50 mg) was dried at 100 °C under ~0.04 mbar overnight in a 25 mL reactor. Under Ar atmosphere, the solvent (0.5 mL, usually 1,2-dichloroethane), the ATB initiator (0.07 mL), and EA (0.5 mL) were added. The mixture was freeze-pump-thaw degassed and exposed to molecular sieve dried IB for 24 h either at an elevated temperature or under UV irradiation. The IB was present in excess and was kept at 1 atm pressure unless indicated otherwise in Table 2 (in runs 15 and 16 it was kept at a few atm pressure and the pressure drop was recorded).

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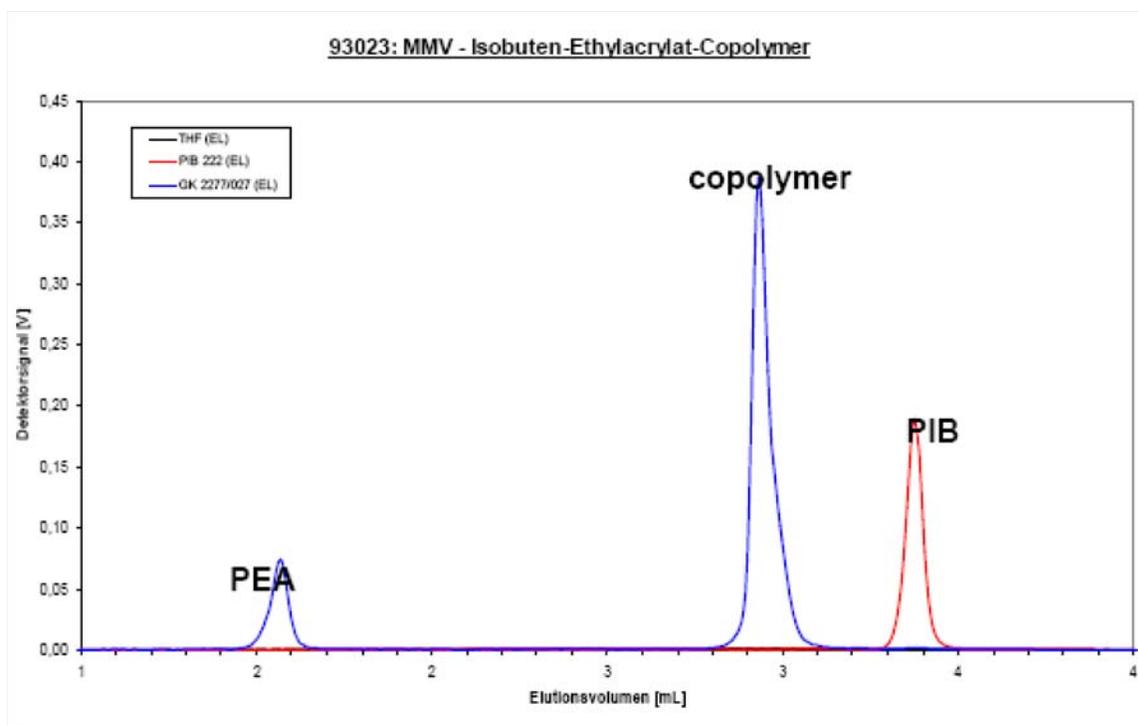
Figure 5. HPLC trace of the reaction mixture from the production of a 1:1 alternating copolymer of IB and EA obtained by BASF under catalysis with EtAlCl$_2$ (see text).

The reaction was then quenched with methanol, the solvents were removed on a rotary evaporator, and the residue was dried on a vacuum line. The product was dissolved in tetrahydrofuran and passed through a column of alumina about five times to remove the bulk of the catalyst. A Soxhlet apparatus was used to recover all polymer from the alumina. The dried polymer was dissolved in CDCl$_3$ for NMR analysis and in tetrahydrofuran for GPC analysis. It was dried in an oven at 80 °C at ~0.04 mbar overnight before TGA and DSC analysis.

The results from a few selected runs are summarized in Table 2, and the characterization of the resulting copolymers is illustrated in Figures 6 - 14 . The gDOSY spectrum in Figures 8 and 14 and the HPLC results in Figures 6 and 10 demonstrate that the material is a true copolymer, and this agrees with the results of thermal analysis. The NMR spectra in Figures 9 - 11 illustrate the presence of a peak that belongs to the copolymer but is absent in the spectrum of the known alternating copolymer (Figure 4), and is attributable to CH groups at branch sites observed in *b*-PIB. However, under certain copolymerization conditions this peak is not present (Figures 13 and 14). A definitive determination of the presence of branches in the copolymer is being sought presently using 2D NMR.

The content of IB in the copolymer is 20 - 30% and we are now looking for conditions that will increase it above 50%.

Table 2. Results of Selected IB-EA Copolymerization Runs under Non-Oxidizing Conditions

Run	P6[a]	P9[a]	P10[b]	P11[b]	P12[b]	P15[c]		P16[c]
Temp (ºC)	80	80	40-50	20	20	80		80
EA (mL)	2.0	1.00	1.00	0.50	0.50	0.55		0.55
IB[d]	Excess	Excess	Excess	Excess	Excess	3.80		3.75
C catalyst (wt%)[e]	1.9	3.0	3.0	4.2	2.7	0		1.0
Initiator (0.07mL)	DTBP	ATB	ATB	ATB	ATB	ATB		ATB
Pressure Change						≈5psi		80psi
DCE (mL)	0.50	0.50	0.50	0.50	1.0	0.50		0.50
Mw		1×10^6	3.6×10^4	2.0×10^4	2.8×10^4	3.3×10^4	300	1.6×10^5
Mw/Mn		2.0-2.5	2.6	2.7	3.5	2.8	1.0	4.63
Tg (ºC)	3.3	-2.5	1.8	-24.3	-9.9			-27.3
T$_d$(ºC)	384	392	365	394	397			399
Molar ratio EA : IB	2.5	1.3	1.2	1.9	1.5			1.7
% of weight (IB)	18	30	32	23	27			24
Yield (%)		24.0	14.6	53.6	24.5			

[a] Thermal initiation. [b] Photoinitiation. [c] Pressure copolymerization. [d] Gaseous IB at 1 atm pressure unless shown otherwise. [e] Catalyst concentration (%) is based on weight excluding IB. For pressure copolymerization, the weight includes IB. Catalyst: 50 mg of LiCB$_{11}$Me$_{12}$.
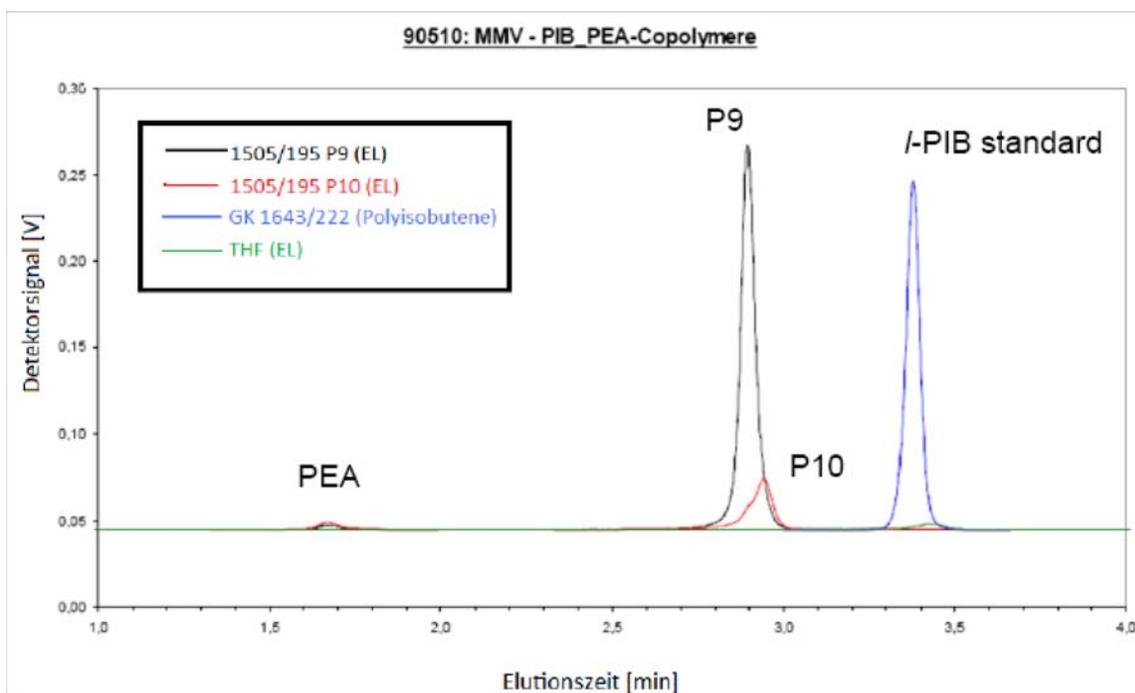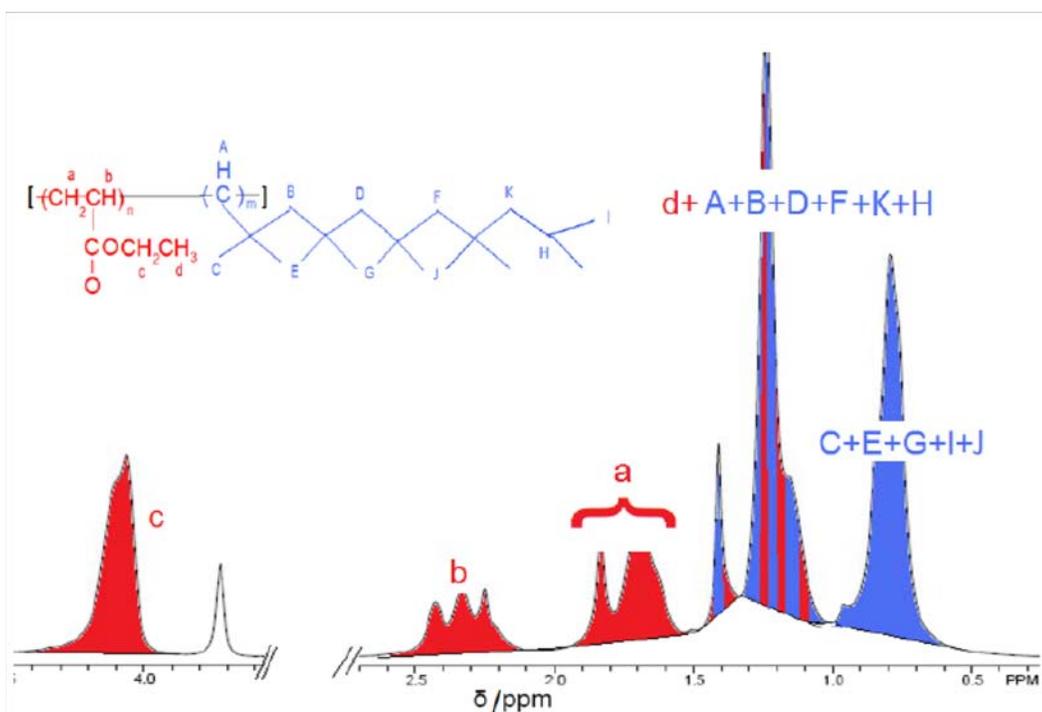

Figure 6. HPLC trace of the reaction mixture from IB-EA copolymerization runs P9 and P10 (see Table 2). Measurement performed by BASF.

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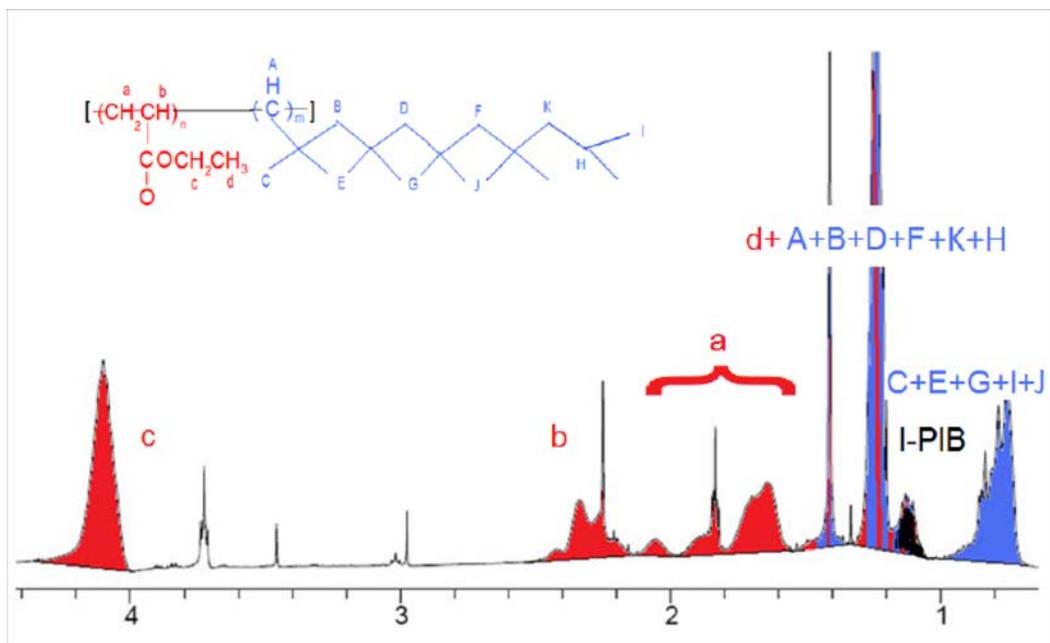
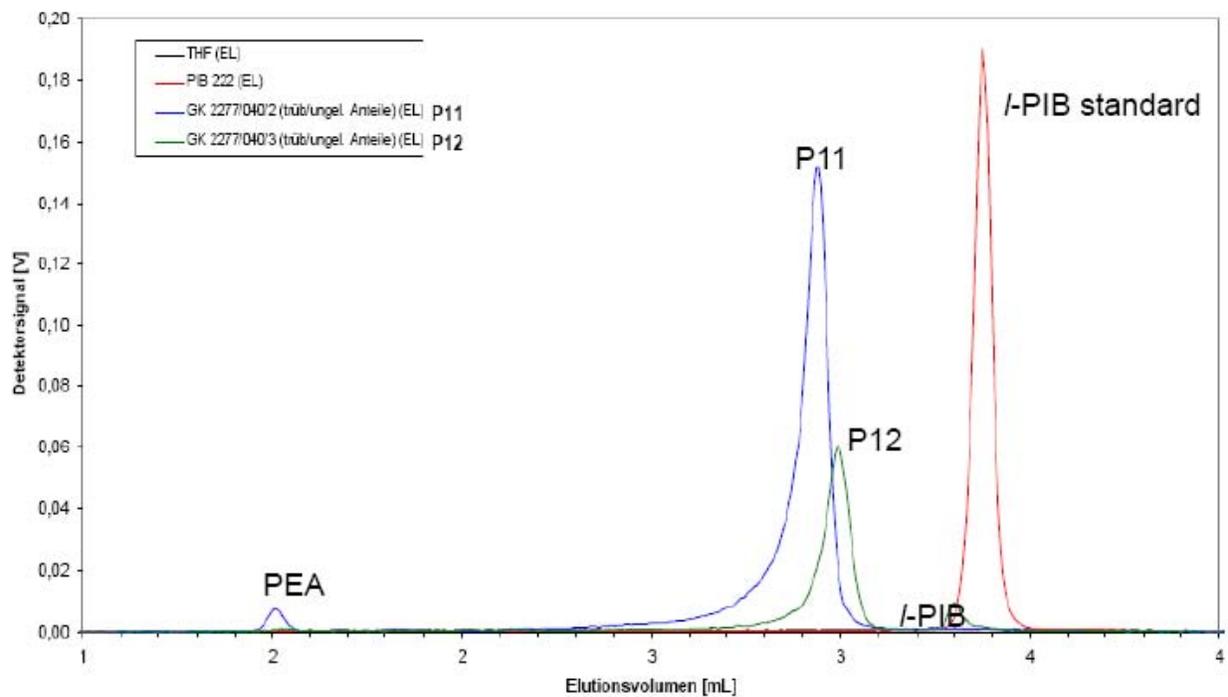**Figure 7**. ^{1}H NMR spectrum in CDCl$_3$ of a copolymer of IB and EA obtained in Run P11.
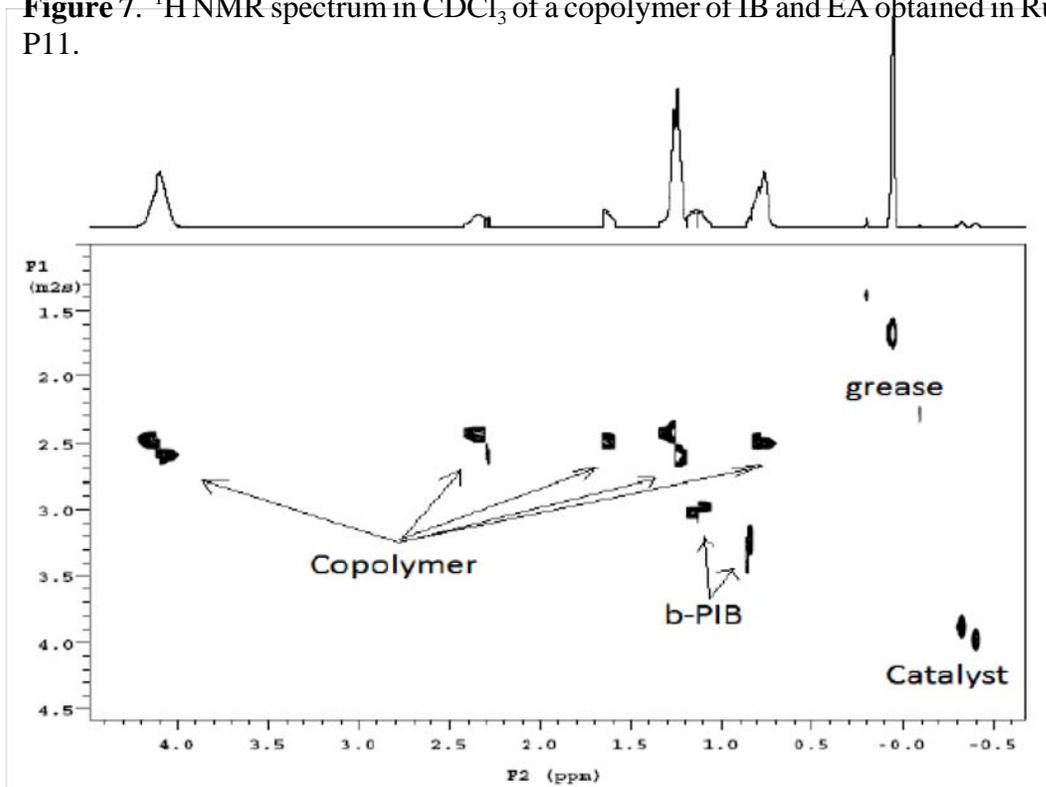
Figure 8. gDOSY ^{1}H NMR spectrum in CDCl$_3$ of a copolymer of IB and EA obtained in Run P11.

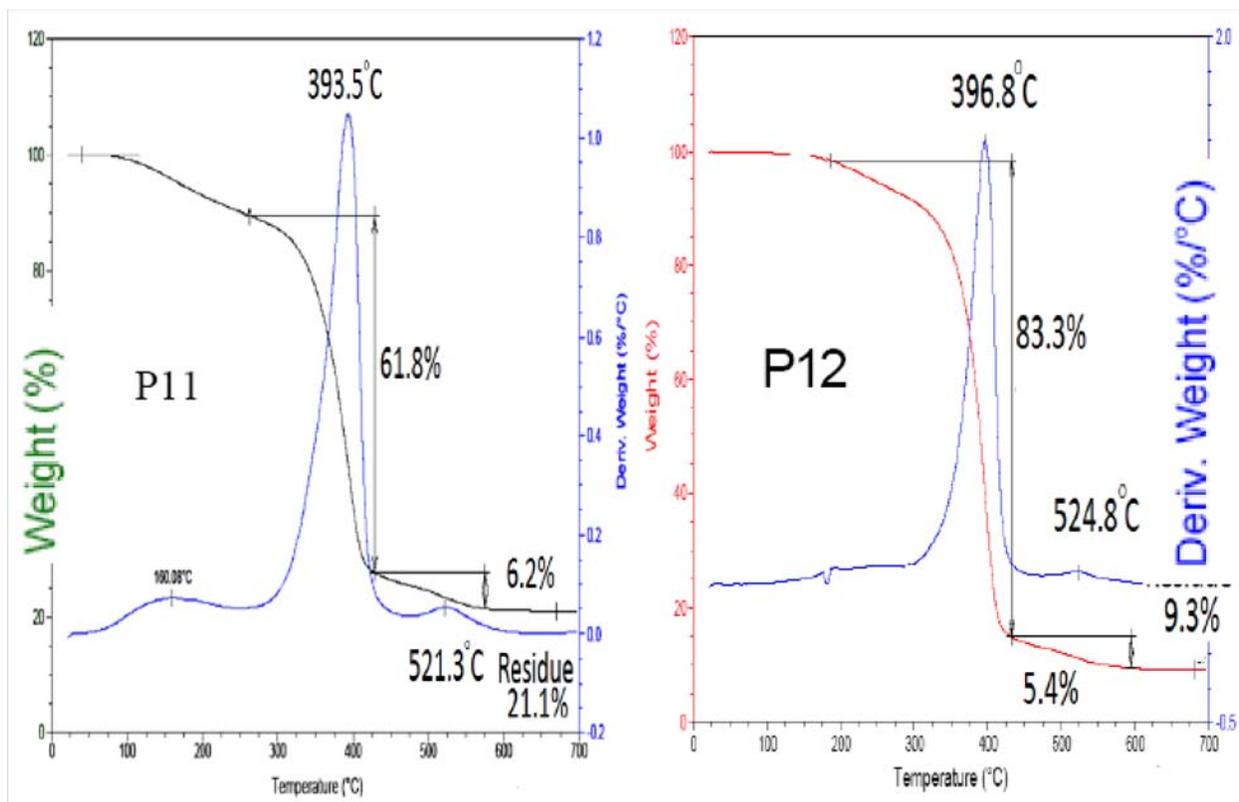**Figure 9**. ^{1}H NMR spectrum in CDCl$_3$ of a copolymer of IB and EA obtained in Run P12.

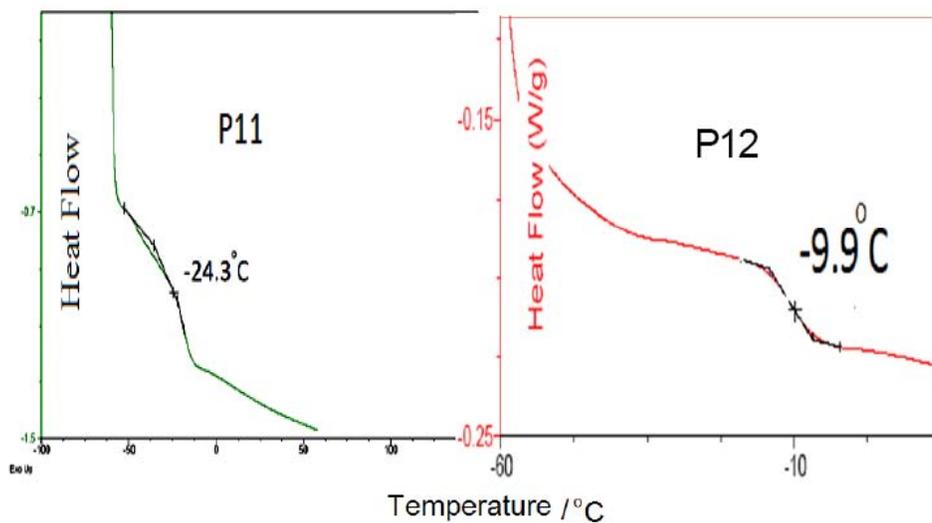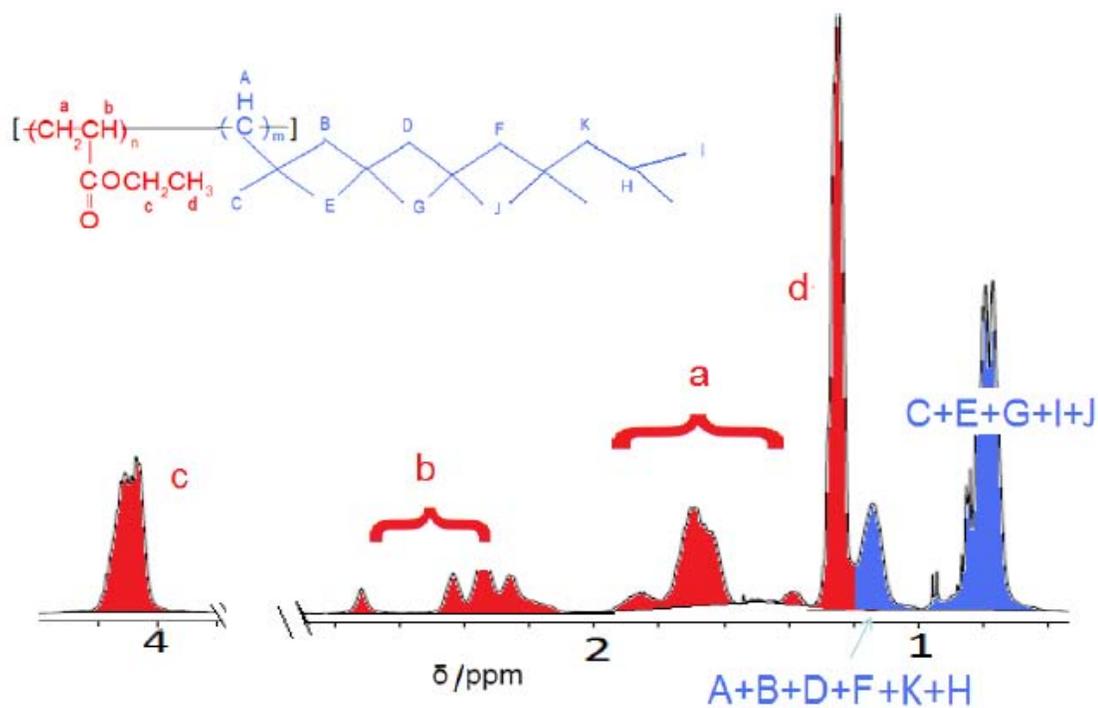**Figure 10**. HPLC trace of the reaction mixture from IB-EA copolymerization runs P11 and P12 (see Table 2). Measurement performed by BASF.
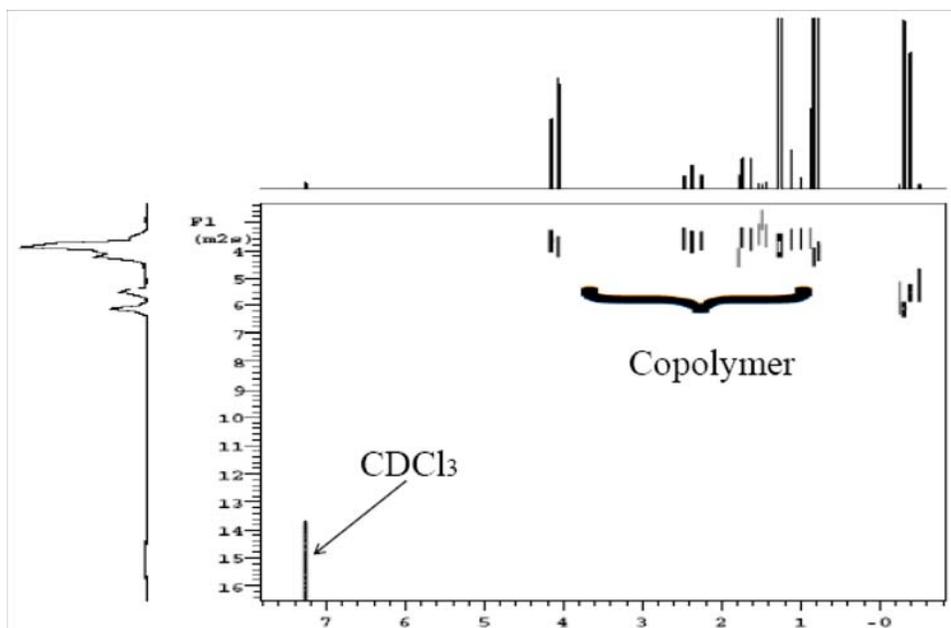
Figure 11. TGA trace of the reaction mixture from IB-EA copolymerization runs P11 and P12 (see Table 2).

Figure 12. DSC trace of the reaction mixture from IB-EA copolymerization runs P11 and P12 (see Table 2).

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Figure 13. ^{1}H NMR spectrum in CDCl$_3$ of a copolymer of IB and EA obtained in Run P16.

Figure 14. gDOSY ^{1}H NMR spectrum in CDCl$_3$ of a copolymer of IB and EA obtained in Run P16.