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Carbocationic Polymerizations for Profit and Fun

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Summary: This presentation consists of two largely independent parts: The first "for Profit" part concerns a bird's eye view of recently commercialized carbocationic processes and materials created by these processes in the author's laboratories whose marketing started during the past ~5 years by various companies. These materials/processes include liquid telechelic polyisobutylene (PIB) for architectural sealants, poly(styrene-*b*-isobutylene-*b*-styrene) (PSt-*b*-PIB-*b*-PSt) triblocks for thermoplastic elastomers, PIB/PSt-based blocks for coating of medical devices, and PIB-based microemulsions for surface protection of painted metal surfaces. It is concluded that in order to enhance and solidify research in polymer synthesis it would behoove the scientific community to pay increased attention to intellectual property protection. Appropriately managed patenting and publishing activities are self-reinforcing and may be quite profitable.

The second "for Fun" part concerns a brief review of the design, synthesis and characterization of two novel fully aliphatic star-block copolymers: $\varnothing$(PIB-*b*-PNBD)$_3$ and $\varnothing$(PNBD-*b*-PIB)$_3$ (where PNBD = polynorbornadiene). The constituent moieties of these star-blocks are identical except their block sequences are reversed. Motivation for the synthesis of $\varnothing$(PIB-*b*-PNBD)$_3$, consisting of a low Tg (~-73°C) PIB inner-corona attached to a high Tg (~320°C) PNBD outer corona, was the expectation that this star-block would exhibit thermoplastic elastomer characteristics, and that it could be used in applications where similar polyaromatic-based TPEs cannot be employed (e.g., magnetic signal storage). The other star-block, $\varnothing$(PNBD-*b*-PIB)$_3$, comprises the same building blocks with the PIB and PNBD sequences reversed. We found that the secondary chlorine at the PNBD chain end, in conjunction with $TiCl_4$, is able to initiate the polymerization of isobutylene. Details of the carbocationic polymerization of NBD, together with the microstructure of PNBD, will be discussed.

Keywords: block copolymers; living polymerization; polyisobutylene; polynorbornadiene; thermoplastic elastomers

I. Introduction

This presentation concerns two main themes: Carbocationic polymerization research for fun and

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[•] Parts of this presentation have been published in references 1 and 2.

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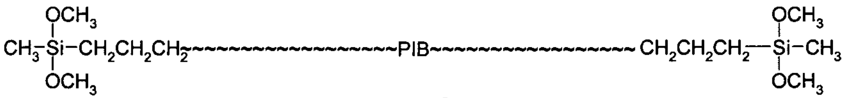
for profit. The first part concerns the **profit** motive and illustrates with a few examples recently commercialized products made by carbocationic processes originally invented and investigated at the University of Akron; subsequently, in the second part we summarize recent **fun** research we carried out to produce novel fully aliphatic star-block polymers.

II. The Lead Question and the Profit Motive

The lead question (you may call it the guiding principle) of our research is this: *How can we translate data into knowledge and knowledge into useful things?* To generate data is relatively easy (any chemist can do a rate study of a methyl, ethyl, isopropyl, t-butyl series). To translate data into knowledge, however, is more difficult; and, ultimately, to upgrade newly generated knowledge to create something useful is extremely difficult. Some research/researchers may never reach this final stage.

Let us start by taking a bird's-eye view of products, recently commercialized by various companies around the world that are based on fundamental knowledge generated in our laboratories. First of all, there is EPION®, introduced in 1997 by Kaneka Inc., of Japan.



$$CH_3-\underset{OCH_3}{\overset{OCH_3}{Si}}-CH_2CH_2CH_2\sim\sim\sim\sim PIB\sim\sim\sim\sim CH_2CH_2CH_2-\underset{OCH_3}{\overset{OCH_3}{Si}}-CH_3$$

EPION®

Epion is a low molecular weight liquid methoxysilane ditelechelic polyisobutylene (PIB) used as architectural sealant. This PIB derivative is obtained by hydrosilation of allyl ditelechelic PIB with methyl dimethoxysilane first described by Wilczek and Kennedy.[3, 4] The combination of properties of hermetic seals of large glass panels used in skyscrapers made with EPION® are superior to other existing sealants, including butyl rubber-based sealants.

Next, we have developed thermoplastic triblock elastomers of poly(styrene-*b*-isobutylene-*b*-styrene) [5, 6] as the cationic chemist's response to anionically prepared poly(styrene-*b*-butadiene-*b*-styrene) (Shell's Kratons). The polyisobutylene-based TPEs exhibit unparalleled oxidative and chemical resistance, combined with outstanding softness and barrier properties, and good processing characteristics. Subsequently, Kaneka Inc. developed a large-scale manufacturing process and proceeded to introduce to the market SIBS (for styrene/isobutylene/styrene) triblocks for various TPE applications.

SIBS

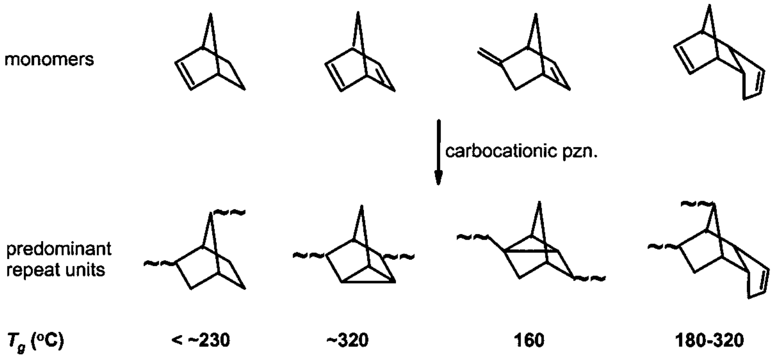
Last but not least, Capital Chemicals Co. recently developed and commercialized POLYPHANE®, a polyisobutylene-based hydrophobizing microemulsion that provides outstanding temporary protection of painted metal surfaces, for example for automobiles, railroad rolling stock, etc.

The major conclusions of the first part of our presentation are that academic research can be quite profitable, and that it would behoove academic researchers to patentably protect their inventions. Inventing useful things can be quite profitable both to the academic inventor and to the industrial developer. Finally, we emphasize that, when properly managed, inventing/patenting for profit, and publishing for fun and toward the advancement of science are highly rewarding self-reinforcing activities. And this thought smoothly leads us to the second part of this presentation:

III. Carbocationic Polymerization of Bicyclic Olefins and the Synthesis of Star-Block Copolymers [1, 2]

III.1. Objectives and Background

Our overall objective was the synthesis of well-defined star-block copolymers that combine soft rubbery PIB segments with hard, high T_g segments of cycloaliphatic polyolefins. Block copolymers comprising soft and hard segments are of great current interest for gaining insight into the structure/property relationship of segmented polymers in general and thermoplastic elastomers (TPEs) in particular. In addition, the envisioned systems are of special interest since both block segments are aliphatic hydrocarbons. Scheme 1 shows the formulae of the monomers considered for these investigations together with the characteristic repeat units obtainable by carbocationic polymerization, and the T_g's of the polymers.



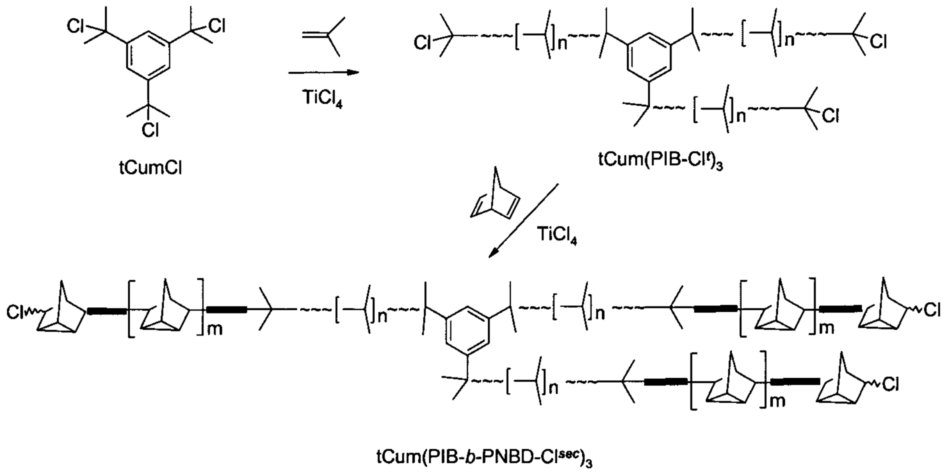
Scheme 1. T_g's of select cycloaliphatic polyolefins

Thus we set out to synthesize two architecturally closely related three-arm star-block copolymers: One consisting of a tricumyl (tCum) core out of which radiate three poly(isobutylene-*b*-cycloolefin) arms, tCum[poly(isobutylene-*b*-cycloolefin)]$_3$, and the other with the block sequence reversed, tCum[poly(cycloolefin-*b*-isobutylene)]$_3$.

Because of their rigid repeat structures, polycycloolefins exhibit a combination of desirable properties, e.g., outstanding chemical resistance, high heat distortion temperature, stiffness and strength, optical transparency, and low dielectric constants.[7, 8] These properties render polycyclooflefins useful for lenses,[9] compact discs,[10] waveguides,[11] photoresists,[12] electronic packaging,[10] medical applications,[9, 10, 13] potential solar energy storage devices,[14] and integrated circuits.[15, 16, 17]

We concentrated our efforts on polynorbornene (PNB) and polynorbornadiene (PNBD), and particularly on the latter which shows the highest T_g reported for hydrocarbon polymers.

Our synthetic strategy included the preparation of a three arm star prepolymer, tCum(PIB-Cl^t)$_3$, followed by the blocking of the second monomer NBD from the active -Cl^t chain ends. Scheme 2 illustrates the synthetic route to tCum(PIB-*b*-PNBD)$_3$. To ensure the envisioned blocking of PNBD, the conditions for the living/controlled polymerization of this cycloolefin were worked out by model experiments (see III.3.).



Scheme 2. Synthetic Strategy for tCum(PIB-*b*-PNBD)$_3$

III.2. Experimental

The materials, equipment, and procedures (both synthetic and characterization) have been described.[1, 2]

III.3.1. Orienting Experiments with Norbornadiene

Preparatory to systematic data gathering, orienting experiments were carried out. The carbocationic polymerization of NBD initiated most likely by adventitious protic impurities in the presence of $AlCl_3$, $AlBr_3$, $MoCl_5$, $MoCl_5/EtAlCl_2$, and Et_3Al, as well as by *tert*-$BuCl/EtAlCl_2$ has been documented.[14, 18, 19, 20, 21, 22] Based on this information and experience with other olefins and diolefins,[23] we decided to examine polymerizations initiated by 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ combinations. TMPCl is an excellent model for the tert-Cl terminus of PIB produced by living carbocationic polymerization.[24] Controlled initiation with TMPCl would yield trimethylpentyl headgroups and thus leads to the possibility of blocking the cyclic olefin from such PIBs.

Based on orientating polymerizations by the use of CH_2Cl_2 diluent, NBD was chosen for further detailed experimentation. Under similar conditions, 2-norbornene (NB) gave substantially lower yields and molecular weights than NBD so that investigations with this monomer were discontinued. In addition, the higher T_g of PNBD prompted us to focus experimentation on this polymer.

III.3.2. Living/Controlled Polymerization of NBD

Efforts were made to develop conditions for the living/controlled carbocationic polymerization of NBD. The effect of monomer concentration, nature of solvents, reagent concentrations and temperature on the rate and molecular weights were explored. Figure 1 (molecular weights vs. conversion and ln([M]$_0$/[M]) vs. time) summarizes the results.

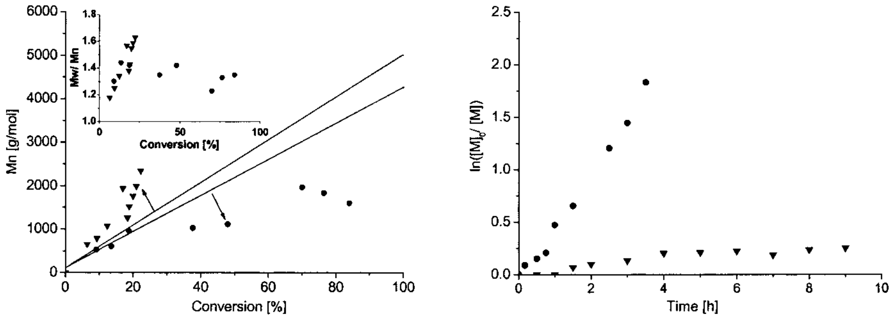


Figure 1. NBD polymerization: M_n vs. conversion (left), theoretical lines assume livingness, inset M_w/M_n vs. conversion; ln([M]$_0$/[M]) vs. time (right); solvent CH_3Cl (●) and $CH_3Cl/CHCl_3$ 30/70 (v/v) (▼)

The series with CH_3Cl (●) was carried out by the use of eight test tubes with: $[NBD]_0$ = 843 mM, [TMPCl] = 18.15 mM, [DtBMP] = 8.9 mM, [DMA] = 32.7 mM, 33 mL CH_3Cl at –60 °C. The precooled coinitiator [$TiCl_4$] = 415 mM was added last. After given time intervals, the reactions were quenched with precooled methanol.

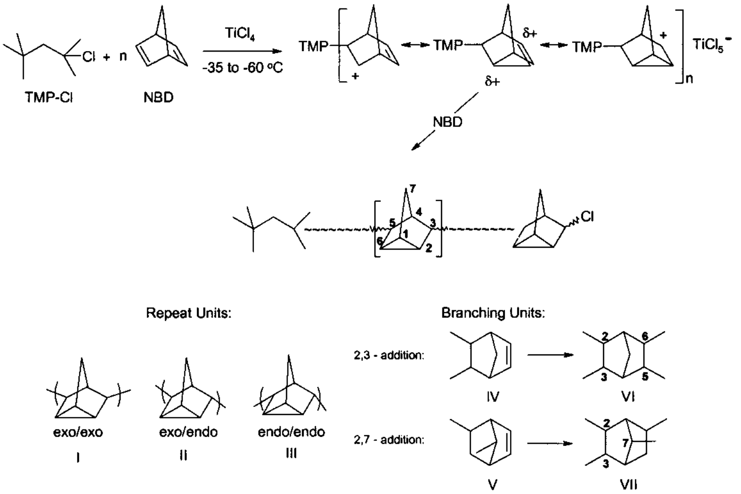
The M_n vs. conversion plot shows M_n's lower than theoretical above ~ 20% conversion, which indicates chain transfer in this region. The corresponding ln ([M]$_0$/[M]) vs. time plot is linear up to ~ 45 min, after which the rate increases significantly. M_w / M_n ~ 1.35 over the entire conversion range (< 84%). According to this evidence the system may be considered living up to ~ 20% conversion.

The series with $CH_3Cl/CHCl_3$ 40/60 (v/v) (▼) was effected with $[NBD]_0$ = 650 mM, [TMPCl] = 12.0 mM, [DtBMP] = 4.9 mM, [DMA] = 21.5 mM, 500 mL $CH_3Cl/CHCl_3$ 40/60 (v/v), -35 °C. The precooled coinitiator $[TiCl_4]$ = 474 mM was added last. After given time intervals, samples were taken and quenched with precooled methanol. These conditions mimic the blocking of PNBD from $\text{tCum(PIB-Cl}')_3$ (see below). The use of this solvent mixture is needed on the one hand to dissolve the high molecular weight monodisperse prepolymer ($CHCl_3$), and on the other hand to provide sufficient polarity (CH_3Cl) for the polymerization of NBD.

The M_n vs. conversion plot shows M_n's above the theoretical line. At low conversions (<23%) this is a signature for slow initiation.[25,26] The M_w/M_n values increase with conversion which is another indication for slow initiation. The induction period in the $\ln([M]_0/[M])$ vs. time plot further confirms slow initiation. Evidently, the low polarity solvent mixture reduces the rate. It is known that even a minor polarity reduction retards living polymerization.[27]

III.3.3. PNBD Microstructure

Scheme 3 helps to visualize the mechanism of initiation and propagation, and shows the repeat structure of PNBD, together with the head- and tail-groups, and branching units.



Scheme 3. Synthesis and Structure of PNBD

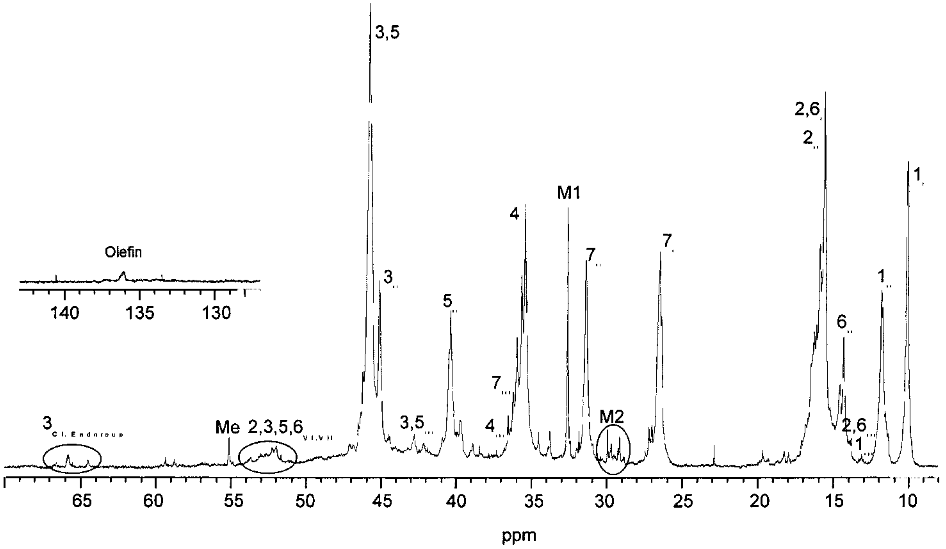
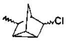


Figure 2. ^{13}C-NMR-Spectrum of PNBD (750 MHz, $CDCl_3$, prepared by TMPCl/$TiCl_4$/CH_3Cl/-60 °C/2h)

The microstructure of PNBD was investigated by ^{1}H and ^{13}C-NMR spectroscopy. Figure 2 shows the ^{13}C-NMR-spectrum of a representative PNBD (M_n = 2250, M_w/M_n = 1.28). The initiator fragment (head-group), tail-group, repeat unit connectivity and branching units were analyzed and identified.

The initiator residue $(CH_3)_3CCH_2C(CH_3)_2$- and the $-CH_2C(CH_3)_2CH_2C(CH_3)_2Cl$ tail group in PIB prepared with TMPCl/$TiCl_4$ have been identified.[28, 29] PNBD obtained by the TMPCl/$TiCl_4$ system shows the three terminal methyl carbons of the head-group (M1) at δ = 32.5, the methylene carbon (Me) at δ = 55.1, and the two adjacent methyl carbons (M2) that produce multiple signals at $\delta \sim 29.5$ ppm. The multiplicity is due to the endo- and exo-positions of the first NBD repeat unit, and to the magnetic nonequivalence of the methyl groups caused by steric congestion.

The  tail-group gives distinctive signals at δ = 64.5 and 65.8 ppm, due to the C^3 bearing the terminal chlorine (exo- and endo-Cl's). According to 2d C-H correlation spectroscopy (750 MHz, $CDCl_3$, not shown) the tail proton bonded to the terminal C^3 resonates at $\delta \sim 3.9$ ppm.

For further details see references 1 and 2.

We obtained M_n = 2,540 g/mol by integrating the ^{1}H NMR spectrum of a representative PNBD (not shown), and M_n = 2,900 g/mol by GPC (RI trace, PIB standards). Integration was effected by relating the intensity of the terminal (C^3) proton signal at ~ 3.9 ppm against the sum of all other protons in the 0.5 – 3.0 ppm range, including the 17 protons in the initiator fragment.

Thus structure analysis by high resolution NMR spectroscopy led to insight regarding repeat unit connectivity, branching, and to a definition of the head- and tail-groups of PNBD prepared by the TMPCl/TiCl4 initiating system.

III.3.4. T_g Versus Molecular Weight

One of the important objectives of our investigations was to prepare PNBDs with T_g's in the 250 – 300 °C range for potential thermoplastic applications. We found conditions under which the molecular weights increased to ~ 2,500 g/mol with increasing conversions (see above). Thus we turned to determine the effect of molecular weight on T_g. Figure 3 shows the T_g as function of PNBD molecular weights.

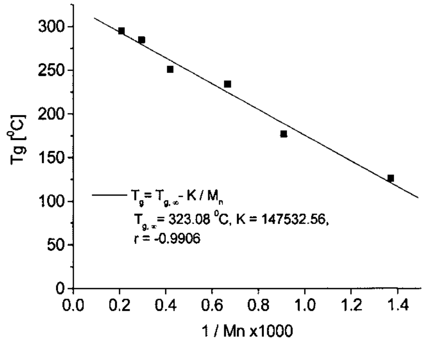


Figure 3. T_g of PNBD as a function of $1/M_n$

Fox and Flory suggested an empirical equation to express the dependence of the T_g on the M_n of different linear polymers: [30, 31, 32]

$$T_g = T_{g\infty} - K/M_n$$

where $T_{g\infty}$ is the T_g of the infinite molecular weight polymer and K is a characteristic material constant. The dependence is due to the decrease in excess free volume, due to chain ends, with increasing chain length.[33] Our data yields $T_{g\infty} = 323$ °C and K = 14.75 x 10^4 (similar to the K values for PVC or PVAc).[34] This $T_{g\infty}$ value is in good agreement with T_g~320 °C published for carbocationically polymerized NBD (M_n 14,970 g/mol $M_w / M_n = 3.73$, polystyrene standards).[35] The agreement between our (extrapolated) and previous literature data suggests very similar microstructures of the PNBDs. This corroborates our conclusions reached by NMR spectroscopy that the microstructures of PNBDs produced by TMPCl/$TiCl_4$ and $AlCl_3$ are very similar.

III.4. Block Copolymerization of Isobutylene and Norbornadiene: Ter- and Star Blocks

III.4.1 Proof of Concept: Novel Linear Triblocks

The initial results by the use of CH_2Cl_2 diluent in model polymerizations were promising. Thus these scouting experiments were extended to blocking NB and NBD from a –Cl^t ditelechelic PIB (dCum(PIB-Cl^t)$_2$: M_n = 5,800 g/mol, M_w/M_n = 1.07 by GPC-LLS; dCum = dicumyl) as initiator under established conditions (Table 1). These trials lead to two novel linear triblocks, PNB-*b*-PIB-*b*-PNB and PNBD-*b*-PIB-*b*-PNBD. DSC-analysis indicated the presence of the T_g's of the hard segments, indicating phase separation.

Table 1. Blocking NB and NBD from dCum(PIB-Cl^t)$_2$

Olefin	Conditions	Results			
	[dCum(PIB-Cl^t)$_2$]/[Olefin]/[$TiCl_4$]/ [DtBP](mmol/L); Solvent, *T*(°C), *t*(h)	Star-Block (g)	M_n (g/mol)	M_w/M_n	$T_{g,\text{hard segment}}$ (°C)
	20.5/ 1380/ 400/ 112; CH_2Cl_2, -60, 3	3.4g	7.1	1.09	118
	20.5/ 813/ 400/ 112; CH_2Cl_2, -60, 3	3.7g	9.1	1.07	218

The synthesis of PNB-*b*-PIB-*b*-PNB and PNBD-*b*-PIB-*b*-PNBD demonstrates that our synthetic strategy conceptualized for the preparation of aliphatic TPEs is indeed operational. These results encouraged us to pursue the controlled synthesis of star blocks.

III.4.2. Synthesis of tCum(poly(isobutylene-*b*-norbornadiene))$_3$

Scheme 2 outlines the strategy for the synthesis of tCum(PIB-*b*-PNBD)$_3$ and shows the structure of the three-arm star-block copolymer. We have demonstrated that the TMPCl/TiCl$_4$ combination efficiently initiates NBD polymerization (see above). Thus we prepared the tCum(PIB-Cl^t)$_3$ macroinitiator by our well-documented technique [36,37] and used it in conjunction with TiCl$_4$ to induce the polymerization of NBD. Preliminary experiments showed that mixtures of polar/ nonpolar solvents (i.e., ~ 50/50 (v/v) CH$_3$Cl/nC$_6$H$_{14}$, CH$_3$Cl/methylcyclohexane (MeCH), CH$_2$Cl$_2$/nC$_6$H$_{14}$, CH$_2$Cl$_2$/MeCH) conventionally used for the preparation of PIB blocks covalently linked to glassy blocks [38] are unsuitable for the envisioned synthesis because NBD polymerizations do not proceed in the presence of even small amounts (~ 20%) of hexanes or MeCH, and because PNBD is insoluble in these aliphatic hydrocarbons. Extended orienting experiments with various solvents and solvent mixtures indicated that under well-defined conditions 30/70 (v/v) CH$_3$Cl/ CHCl$_3$ mixtures at –35 °C gave satisfactory blocking. CHCl$_3$ is a solvent for high molecular weight narrow polydispersity PIB and keeps the tCum(PIB-*b*-PNBD)$_3$ in solution at –35 °C even in the presence of 30% CH$_3$Cl. At higher CH$_3$Cl concentrations (i.e., 40/60 (v/v) CH$_3$Cl/CHCl$_3$) or at lower temperatures (i.e., -45 to -55 °C) the PIB prepolymer precipitated from solution. Thus, satisfactory star-block syntheses could be effected with 30/70 (v/v) CH$_3$Cl/ CHCl$_3$ at –35 °C; under these conditions all the species of a charge (i.e., prepolymer, star-block, and PNBD byproduct (see below)) are in solution, and the 30% CH$_3$Cl provides sufficient polarity for cationic blocking.

In a representative synthesis 25 mL precooled TiCl$_4$ were added to a mixture of 5 g prepolymer (M_n ~ 102,000 g/mol, $M_w / M_n = 1.03$), 20 mL NBD, 0.5 g DtBMP, 1 mL DMA in 700 mL 30/70 (v/v) CH$_3$Cl/ CHCl$_3$ at –35 °C. After 1 h additional 25 mL precooled TiCl$_4$ were added. The reaction was quenched after 10 h by precooled methanol. Under similar conditions, blocking of PNBD did not occur using 50/50 (v/v) mixtures of hexanes/CH$_3$Cl, methylcyclohexane/CH$_3$Cl, and CH$_2$Cl$_2$/CH$_3$Cl. The solubility of the macroinitiator was much lower in CH$_2$Cl$_2$ than in hexanes, MeCH or CHCl$_3$.

The molecular weight of the prepolymer increased to M_n = 107,300 – 109,200 g/mol with exceptionally low values for M_w/M_n (~ 1.01).

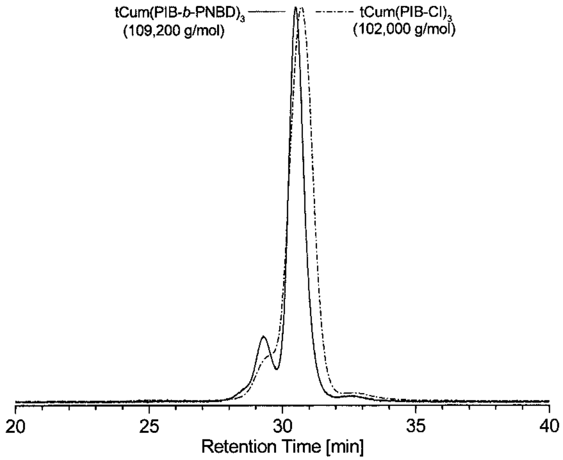


Figure 4. GPC traces of tCum(PIB-Cl^{t})$_3$ and tCum(PIB-b-PNBD)$_3$ (LLS detector)

Figure 4 shows the GPC trace of a prepolymer together with the corresponding star-block. The small but distinct shift of the peak associated with the prepolymer toward lower elution counts after blocking with NBD (i.e., from ~ 30.8 to 30.5 min) indicates blocking of a small amount of PNBD.

In addition to the main peak at ~ 30.8 min associated with the star-block, non-purified polymerization products showed a peak at ~ 39 min, indicating the presence of PNBD homopolymer (M_n ~ 1,600 g/mol (M_w/M_n = 1.28; RI – detector, linear PIB standards) most likely formed by chain transfer. The homopolymer can be removed by precipitation (from THF into ice-cold 1,2-dichloroethane), and essentially uncontaminated, pure star-block can be obtained after two precipitations.

The position of the peak due to the prepolymer suggests M_n =102,000 g/mol, $M_w/M_n \approx$ 1.03 (LLS – detector). In line with this GPC analysis the arm molecular weight of the prepolymer is ~ 34,000 g/mol. The position of the peak due to the star-block suggests M_n =109,200 g/mol, M_w/M_n $\approx$ 1.01. The shoulder at ~ 29 min indicates the presence of a small amount of a species of M_n ~ 206,000 g/mol, i.e., about double that of the prepolymer. This species most likely arose by star/star coupling. In this process a growing arm intramolecularly cationates an arm of another star with a -CH_2-$C(CH_3)$=CH_2 terminus formed by chain transfer (i.e., dehydrochlorination) of a

$CH_2C(CH_3)_2Cl$ terminus. Such star/star coupling reactions were observed previously.[39,40] The very small hump centered at ~ 33 minutes (~ 43,000 g/mol) may be due to a very small amount of product formed by premature chain breaking during star formation.

The molecular weight increase from the prepolymer to the star-block is ~ 7,200 g/mol which is equivalent to an increase of ~ 2,400 g/mol per arm in the star-block. The latter value is comparable to the molecular weight of the PNBD homopolymer contaminant. Thus GPC analysis suggests a star-block consisting of $M_{n,\,\mathrm{PIB}}$ = 34,000 and $M_{n,\,\mathrm{PNBD}}$ = 2,400 g/mol per arm.

III.4.3. Microstructure of tCum(poly(isobutylene-*b*-norbornadiene))$_3$

The microstructure of tCum(PIB-*b*-PNBD-Cl^{sec})$_3$ was investigated by NMR spectroscopy. Figure 5 shows the ^{1}H-NMR spectrum of a representative star-block and of the prepolymer, together with assignments.

The high resolution allowed the detection and quantitative analysis of the aromatic initiator fragment and chlorine-containing tail-groups in both the prepolymer and the star-block, despite their relatively high M_n's. On hand of this information it was possible to calculate molecular weights from ^{1}H-NMR data.

In the prepolymer, the resonance Ar at δ = 7.14 ppm is due to the three aromatic protons of the cumyl initiator fragment. The six (per arm) methyl protons (a) resonate at δ = 0.81 ppm. The terminal methyl and methylene protons (e and d) resonate at δ = 1.70 and δ = 1.98 ppm. It is possible to assign signals for the methyl protons of the tricumyl core (tCu at δ ~ 1.83) but not the adjacent methylene units, because the resonances of the latter are too near the large resonances from the methylene and methyl protons (b and c) of the IB repeat units.

In the star-block, the PNBD-Cl^{sec} terminus is a tricyclic structure with a chlorine in the 3 position. The proton adjacent to this Cl may be in exo or endo position with signals appearing in the δ = 3.8 – 4.0 ppm range. While the signals are, of course, weak and do not allow exo/endo resolution, they are clearly discernible. The assignment of this terminal proton is discussed above.[1]

According to quantitative NMR spectroscopy [1,2] the depicted three-arm star-block consists of a tricumyl core out of which emanate three PIB-*b*-PNBD-Cl^{sec} branches composed of $M_{n,\mathrm{PIB}}$ = 34,500 and $M_{n,\,\mathrm{PNBD}}$ = 2,100 g/mol, abbreviated by tCum[PIB(34.5K)-*b*-PNBD(2.1K)-Cl^{sec}]$_3$.

The molecular weights determined by proton NMR spectroscopy are in excellent agreement with those determined by GPC, i.e., $M_{n,\text{ prepolymer}}$ = 103,900 and 102,000 g/mol, and $M_{n,\text{ star block}}$ = 110,100 and 109,200 g/mol, respectively.

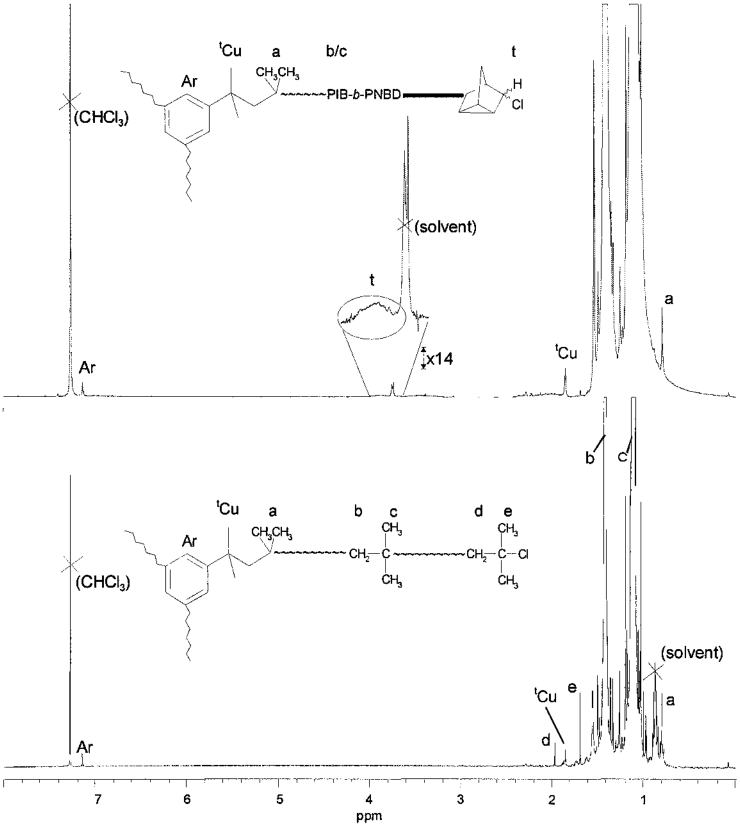
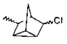
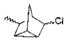


Figure 5. ^{1}H NMR spectra of tCum(PIB-Cl^t)$_3$ and tCum(PIB-b-PNBD-Cl^{sec})$_3$ with assignments (750 MHz, $CDCl_3$)

III.4.4. Synthesis of tCum[poly(norbornadiene-*b*-isobutylene)]$_3$

The synthetic strategy for the synthesis of tCum(PNBD-*b*-PIB-Cl^t)$_3$ was essentially the same as in the case of tCum(PIB-*b*-PNBD-Cl^{sec})$_3$, except that the sequence of blocking was reversed: the polymerization of NBD was effected by the tCumCl/$TiCl_4$ combination and, subsequently, the tCum(PNBD-Cl^{sec})$_3$ prepolymer was used, in conjunction with $TiCl_4$ to induce the polymerization of IB. The first step of the synthesis was the preparation of the three-arm star tCum(PNBD)$_3$ prepolymer. On the basis of our experience with the TMPCl/$TiCl_4$ system (see above), we expected and indeed found that tCumCl readily induces NBD polymerization in the presence of $TiCl_4$. The resulting tCum(PNBD-Cl^{sec})$_3$ showed M_n ~ 2,900 g/mol (RI-detector, against PIB standards).

The second step, the blocking of IB from the  terminus, also proceeded with ease. It is of interest that this *sec*-chlorine initiates IB polymerization because the structurally similar isopropyl chloride is an inefficient initiator under similar conditions.[41] The ease of initiation with  is most likely due to the strained tricyclic structure.

The molecular weight of the star-block was ~ 14,200 g/mol (M_w/M_n ~ 1.99). That suggests ~ 900 g/mol per inner PNBD arm and 3,800 g/mol per outer PIB arm: tCum(PNBD(0.9K)-*b*-PIB(3.8K))$_3$.

III.4.5. Microstructure of tCum[poly(norbornadiene-*b*-isobutylene)]$_3$

Figure 6 depicts the ^{1}H-NMR spectrum of the star-block, together with relevant assignments. The resonances at δ = 1.98 and 1.68 ppm (c and d) indicate the presence of the terminal methylene and methyl protons, respectively. The PNBD segments are not resolved under the dominating methyl and methylene signals (a and b) of the PIB segments but base broadening of these signals (in the 0.8 – 1.8 ppm range) clearly suggests the presence of PNBD. The signal for the aromatic protons (Ar) is not resolved either, despite the high magnetic field applied. The rigid PNBD segments may cause signal broadening by strain on the core as suggested by signal intensity in the 7.1 – 7.25 ppm range. The presence of a weak broad signal (t) at δ ~ 3.9 ppm is due to unreacted PNBD chain ends (for a detailed analysis see above) and suggests inefficient initiation. The resolution of the signals is insufficient for a quantitative evaluation of the repeat structure.

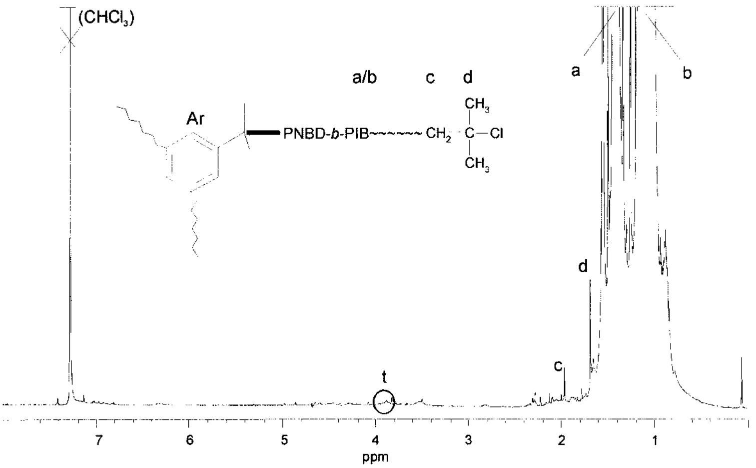


Figure 6. ^{1}H NMR spectrum of the star block tCum[PNBD(0.9K)-*b*-PIB(3.8K)]$_3$ (750 MHz, $CDCl_3$)

III.5. Thermal Characterization of the Star Blocks

Both tCum(PNBD-*b*-PIB)$_3$ and tCum(PIB-*b*-PNBD)$_3$ showed two T_g's, indicating the separation of rubbery and glassy phases (Figure 7).

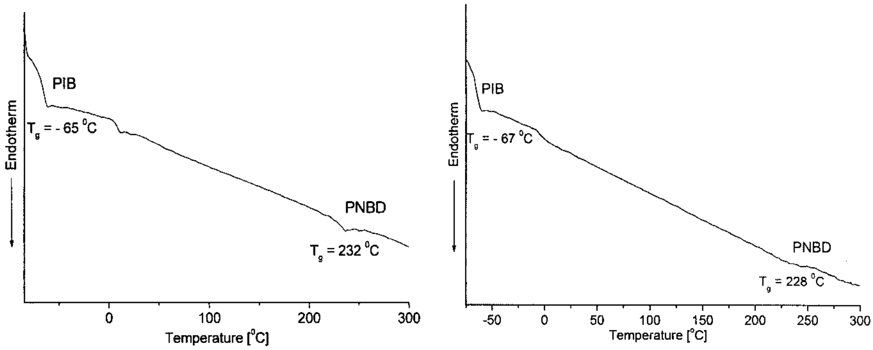


Figure 7. DSC thermograms of tCum(PIB-*b*-PNBD)$_3$ (left) and tCum(PNBD-*b*-PIB)$_3$ (second heating, M_n's = 109,200 (GPC-LLS) and 14,200 g/mol (GPC-RI) respectively)

The DSC thermogram of tCum[PIB(34.5K)-*b*-PNBD(2.1K)]$_3$ showed one transition at ~ -65 °C due to the PIB phase and another at ~ 232 °C which is associated with the glassy PNBD domains. The transition at ~ 0 °C is most probably due to moisture. The presence of the two transitions indicates phase separation, which is remarkable in view of the relatively low molecular weight of the PNBD segments. With the Fox-Flory relationship (see above), the T_g ~ 232 °C for the PNBD in the star-block corresponds to M_n ~ 1,620 g/mol. This value is somewhat lower than those calculated from NMR and GPC data (i.e., NMR gives ~ 253 °C for M_n ~ 2,100 g/mol; GPC gives ~ 263 °C for M_n ~ 2,400 g/mol).

The DSC thermogram of tCum[PNBD(0.9K)-*b*-PIB(3,8K)]$_3$ also showed two T_g's, one at - 67 °C, marking the rubbery PIB phase, and another at 228 ^{0}C, indicating the presence of the glassy PNBD phase. It is surprising to observe this phase separation, considering that the relatively small rigid PNBD inner core would be expected to be masked by the voluminous PIB outer core. With the Fox-Flory relationship (see above), the T_g ~ 228 ^{0}C for the PNBD phase would correspond to M_n ~ 1,560 g/mol. This value is similar to the PNBD molecular weight between two PIB blocks: I.e., each arm of the star-block bears a PNBD segment af ~900 g/mol. Two PNBD segments are connected via the cumyl core of the star-block.

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