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Polyisobutylene Based Supramolecular Networks via Living Carbocationic Polymerization

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Summary: Functionalized, styrene based monomers were investigated for copolymerization with isobutylene (IB) via living carbocationic polymerization. The achieved incorporation of polar moieties into the polymer backbone yielded supramolecular networks, which were analyzed and characterized via rheological measurements.

Keywords: living carbocationic polymerization; polyisobutylene; supramolecular networks

Introduction

Isobutylene (IB) can be polymerized by living or nonliving cationic polymerization.[1] As the monomer itself is limited in structural variability, modifications of PIB can be introduced into the polymer by modifications at the starting[2,3]- or end-group[4–8] moieties as well as via a direct copolymerization of IB with monomers subjectable to cationic polymerization like styrene[9] and vinyl ethers[10] yielding either statistical- or blockcopolymers.

The present work investigates the direct copolymerization of IB with polar monomers or other monomers further subjectable to modification via azide/alkine-"click"-reaction using the living cationic polymerization with $TiCl_4$/2,4,4′-trimethylpentan-chloride (TMPCl) as initiator. The chlorine (**1a**)-, azido (**1b**)- or alkynyl (**1c**)-moieties enable a subsequent modification via the azide/alkine-"click"-reaction, whereas a polar moiety is attached in monomers **2** and **3** via a styrene moiety (see Scheme 1). Polar moieties such as thymine (**2**) and pyridine (**3**) units are investigated for the direct introduction of polar monomers. In comparison, additional information on the copolymerization is obtained by inline-IR monitoring of the polymerization kinetics, comparing the polar monomers with the structurally related polar additives such as picoline.

Experimental Part

Materials

For the syntheses of the monomers **1b**, **1c**, **2** and **3**: THF was dried over KOH and freshly distilled from Na and benzophenone prior use. 4-Vinylbenzylchloride **1a** was distilled from CaH_2 prior use.

For the polymerizations, solvents, initiator and IB were prepared as described in previous publications.[11] All other reagents were used as received from Sigma Aldrich.

Syntheses of Comonomers

The syntheses of 4-vinylbenzylazide (**1b**), (1-(1-(4-vinylbenzyl)-1H-1,2,3-triazol-4-yl)-methylene-5-methylpyrimidine-2,4(1H,3H)-dione) (**2**) and (4-pyridylethyl)-4-vinylbenzene (**3**) were carried out as described in literature.[11] 4-(trimethylsilyl)ethynylstyrene (**1c**) was synthesized according to literature.[12]

Polymerization

The polymerizations of IB with monomers **1** to **3** (see Scheme 2) were carried out under an inert atmosphere of argon. To a solution of hexane, DCM (60: 40, v:v) with N,N-dimethylacetamide (DMA) ($c = 4.4 \times 10^{-3}$ mol/l), DtBP ($c = 2.5 \times 10^{-3}$ mol/l), the comonomer **1–3** and 2-chloro-2,4,4-trimethylpentane (TMPCl) ($c = 0.02–0.002$ mol/l) was

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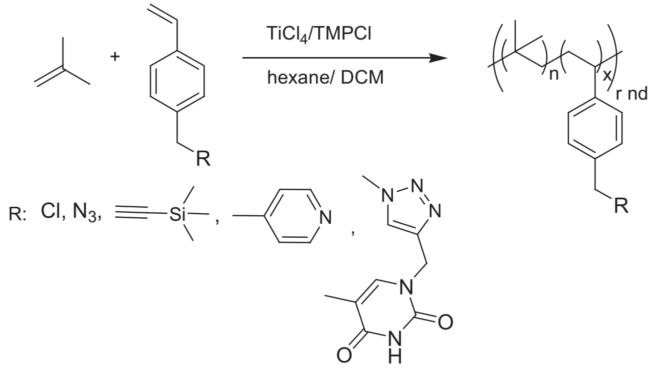


Scheme 1.
Copolymerization of isobutylene with polar styrene-derivatives.

added. After the polymerization mixture was cooled to reaction temperature of (−80 °C) liquid IB (c = 1.2 mol/l) was added. Subsequently, the polymerization was started by addition of $TiCl_4$ (c = 0.124 mol/l).

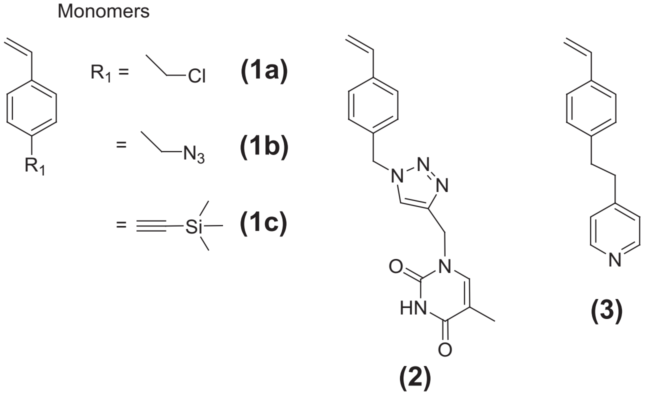
The polymerization was quenched with distilled methanol or allyltrimethylsilane (ATMS) after complete IB conversion was reached (as judged by inline-IR-spectroscopy) and the polymer was subsequently precipitated into a mixture of acetone/methanol = 50:50 v:v.

Instrumentation

Polymer-characterization (NMR-analyses, GPC-measurement and IR-measurement) were done according to literature.[11] Rheological measurements were performed on an Anton Paar (Physica) MCR 501 using parallel plates (diameter 8 mm). The sample temperature was regulated by thermoelectric cooling/heating in a Peltier chamber under a nitrogen atmosphere. At each temperature the sample was equilibrated for 20 min before the measurement started. All measurements were performed in the dynamic mode using a frequency sweep in range from 0.001 to 100 1/s.

Results and Discussion

The polymerization of IB with the different co-monomers **1a–3** (see Scheme 2) was performed in dichloromethane/n-hexane 40:60 (v:v) using an initiator system of



Scheme 2.
Monomers used for the copolymerization (monomers **1a** – **1c**, **2**, **3**) with IB.

$TMPCl/TiCl_4$ and 2,6-di-*tert*-butylpyridine as a proton trap at −80 °C. The comonomers were used in amounts of 1 to 10 mol% relative to IB. All polymerizations were monitored via inline-ATR-FT-IR spectroscopy, the so obtained kinetic values were determined by first-order kinetic plots ($\ln[M]_0/[M]_t$ vs. time (t)). (see eqs. 1–2).

$$\ln [M]_0/[M]_t = k_{app}\, t \qquad (1)$$

$$k_{app} = k_p\, K_{eq}\, [I]_0\, [LA]_0^2 \qquad (2)$$

Calculation of k_p was then accomplished according to eq (2) using $k_{-i} = 7.5 \times 10^7$ 1/s and $k_i = 15$ 1/(s.M^2) according to Storey et al.[13] as shown in Table 1. Results of the polymerization using monomer **3** (1 mol%) in dependence to the initiator concentration and in comparison to the polymerization of IB with picoline used as additives for comparing their kinetic behavior are summarized.

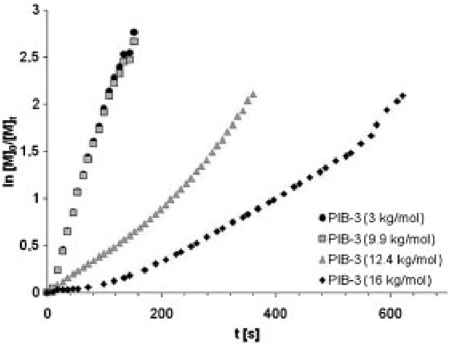


Figure 1.
First-order kinetic plot of the copolymerizations of IB with **3** using different initiator concentrations.

The copolymerization of IB with **3** up to 10.000 g/mol yielded results interpretable as a controlled polymerization, generating PIB with narrow molecular weight distribution as well as molecular weights meeting expectations (Table 1, entry 1 and 2; indicating already published values[11] shown for comparison with the new results). First order kinetic plots indicated a linear consumption of monomer as shown in Figure 1 when plotting $\ln(M_o/M_t)$ vs. time. However a further increase of the molecular weight up to 30.000 g/mol could not be reached, although the molecular weight distributions remained narrow (PDI = 1.2–1.4) and the propagation rate constant was comparable to those observed for a projected $M_n = 3{,}000$ g/mol. The absence of terminations reactions was proven by the linear dependence of the first-order kinetic plots from $M_n = 3{,}000$ to $M_n = 16{,}000$ g/mol (Table 1, entry 1–4), shown in Figure 1. Incorporation of **3** was achieved in amounts of ∼ 1 mol% of comonomer **3**. Comparing results of a polymerization reaction using picoline as additive instead of **3** in a similar amount showed an uncontrolled polymerization at both, lower and higher projected molecular weights with larger molecular weight distributions (1.5 to larger than 2.1).

For the copolymer of PIB-**3**, (see Table 1 entry 2) containing 1 mol% of **3** and a

Table 1.
Polymerization carried out with IB and monomers **3** (1 mol%) in comparison with a polymerization of IB in presence of picoline (1 mol%).

entry	monomer/additive	M_{calc}	M_n GPC	M_w/M_n	k_{app} (s^{-1})	Yield (%)	k_p ($10^8\ s^{-1}M^{-1}$)	Incorp. (mol%)
1	**3**	3,000	2,800	1.4	0.0194	80	2.57	1
2		10,000	9,900	1.3	0.0171	86	7.67	1.1
3		20,000	12,400	1.3	0.00512	80	2.88	1
4		30,000	16,000	1.2	0.00281	76	2.04	0.8
5	picoline	3,000	3,100	1.5	0.0416	90	5.84	–
6		10,000	7,600	1.6	0.01156	85	3.98	–
7		20,000	28,700	1.5	0.00175	87	2.28	–
8		30,000	190,900 13,100	1.1 2.1	0.004514	70	6.14	–

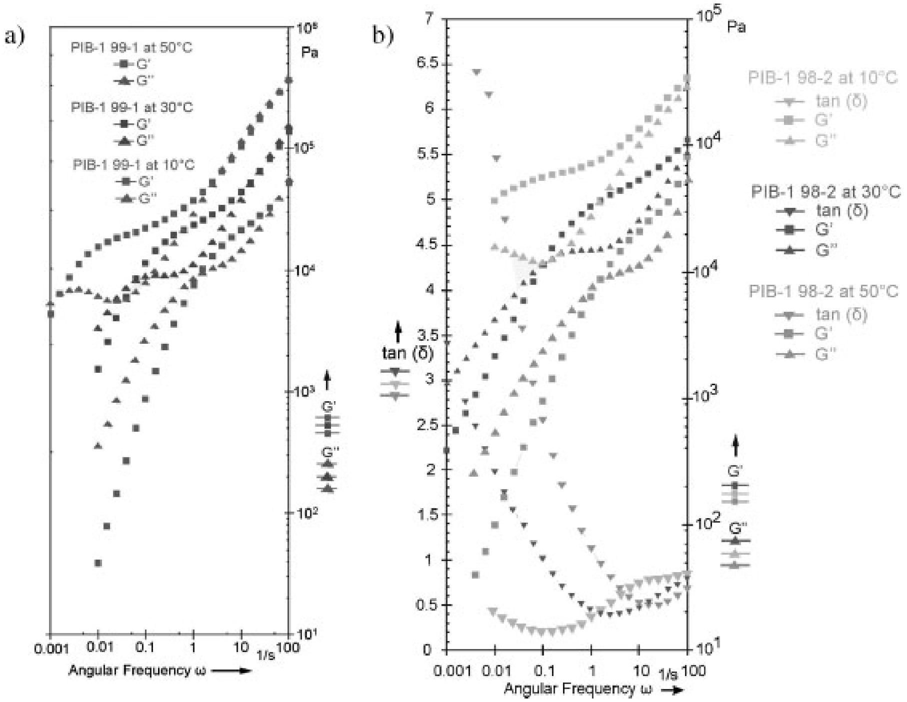


Figure 2.
Melt rheology for the copolymers of IB with a) 1 mol% and b) 2 mol% of **3**.

copolymer PIB-**3** containing 2 mol% in the same range of the molecular weight,[11] melt rheological behavior was studied[14] in order to check for network-formation via hydrogen bonds (see Figure 2).

Figure 2 showed a significant change of the rheological behavior upon incorporation of 1 and 2 mol% of the polar comonomer **3**, in comparison to pure PIB (Newtonian flow), yielding a crossover of G″ and G′, indicative of a rubbery plateau. This rubbery plateau clearly indicates interactions between the polymer chains on the basis of hydrogen bonds interacting between the polymer chains, as well as interations between the aromatic rings introduced via the comonomers themselves.

To intensify the effects of the comonomer on the polymer behavior, the incorporation of the comonomer **3** was tested at increased amounts of up to 5-10 mol %.[11] However, as this approach was not successful for both monomers, monomer **3** and the collidine functionalized styrene (comonomers **1a** - **1c**) were probed as comonomers for introducing functionalization into the PIB chain after the polymerization reaction via the azide/alkine-“click”-reaction. The results of these copolymerizations are shown in Table 2.

Copolymerization of **1a** with IB was not controlled yielding a bimodal molecular weight distribution, however yielding an incorporation of ~ 6 mol% according to NMR-spectroscopy.

Using **1b** and **1c** the copolymerizations with IB were accomplished yielding copolymers with narrow molecular weight distribution and negligible chain transfer (M_n (GPC) = M_n (NMR)), incorporating 0.25–1.0 mol% of the comonomers **1b** and **1c**, respectively. In view of the high amounts of the comonomers used during the copolymerization (5 to 10 mol% of **1b**) (see entries 3 and 4) the low incorporation statistically leads to less than one comonomer within one polymer chain. In Figure 3

Table 2.
Results of copolymerizations with IB and monomer **1a** (10 mol%) **1b**, **1c** (1, 5 and 10 mol%) and **2** (10 mol%)

Entry	Comonomer	Mol%	M_n GPC	M_w/M_n	M_n NMR	Incorp. %
1	**1a**	10	9,800	9.8	3,500	~ 6
			8,000	2.7		
2	**1b**	1	5,600	1.5	5,600	1
3		5	10,000	1.5	10,100	0.5
4		10	5,800	2.5	6,200	0.25
5	**1c**	1	10,400	1.5	10,400	0.8
6		5	8,300	1.3	13,500	<0.25
7	**2**	10	5,500	1.5		<0.1

the incorporation of 1 mol% of **1b** and up to 0.8 mol % of **1c** into the PIB chain was proven via ^{1}H-NMR spectroscopy (see Table 2, entries 2 and 5). via ATR-FT-IR spectroscopy of the copolymer. However, a further increase of the incorporation above the achieved ~ 1 mol% functionalization into the PIB chain could also not be achieved with **1b** and **1c**.

Conclusion

It has been demonstrated that the copolymerization with pyridine substituted styrene monomer **3** and IB could be achieved in amounts of up to 2 mol% via a living carbocationic polymerization reaction. The incorporation of monomer **3** lead to a significant change in the rheological behavior of the resulting copolymers, thus proving the presence of the supramolecular interactions between the polymer chains as analyzed by the observed rubbery plateau. The azide- and alkine-substituted styrene comonomers **1b** and **1c** were incorporated into PIB chains in amounts of up to 1 mol%, thus in the future permitting further functionalization of the copolymer chains with ligands not subjectable to the direct copolymerization. The present method allows a simple functionalization of PIB with polar ligands, thus allows introducing new functionalities as well as thermoplastic properties into this highly versatile and biocompatible polymer.

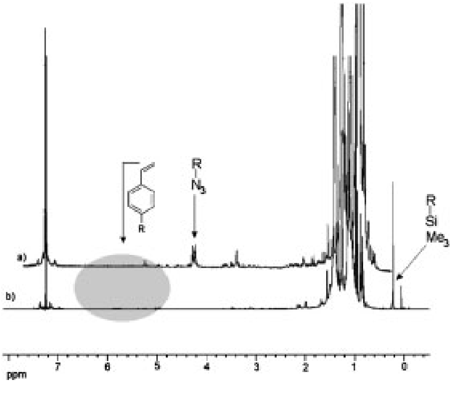


Figure 3.
^{1}H-NMR-spectra of a) IB copolymerized with 1 mol% of **1b** (see Table 2 entry 2) and b) IB copolymerized with 1 mol% of **1c** (see Table 2 entry 5).

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