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Living carbocationic polymerization

LIV. Blocking efficiency in diblock copolymerization of isobutylene – methyl vinyl ether*

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Summary

Diblock copolymers of isobutylene (IB) - methyl vinyl ether (MeVE) have been prepared by sequential monomer addition by employing 2-chloro-2,4,4-trimethylpentane (TMPCl)/$TiCl_4$ initiating system in the presence of nBu_4NCl or dimethylacetamide (DMA) in CH_2Cl_2/hexanes at -80°C. In line with our earlier observations (1), living carbocationic polymerizations (LC$^{\circledR}$Pzn) were obtained in the presence of nBu_4NCl (i.e., the molecular weight of the poly(vinyl methyl ether) segment increased upon $TiCl_4$ addition), however, extensive chain transfer occurred in the presence of DMA. According to column chromatography analysis, the product prepared in the presence of nBu_4NCl is essentially pure PIB-b-PMeVE diblock (~96w%) contaminated with a very small amount (~4w%) of PIB. In contrast, the product obtained with DMA contains only ~21w% PIB-b-PMeVE together with ~72w% PIB and ~5w% PMeVE homopolymers. This large difference in blocking efficiencies suggests that the structures of the growing species are different in the presence of the common anion salt, $\underline{n}Bu_4NCl$, and the electron donor, DMA.

I. Introduction

Recently we have described the first synthesis of a polyolefin-poly(alkyl vinyl ether) diblock, i.e., PIB-b-PMeVE, by LC$^{\circledR}$Pzn using the sequential monomer addition technique (1). While close to theoretical blockings were obtained in the presence of nBu_4NCl, ill-defined discolored products arose by the use of DMA. The purpose of this communication is to confirm the earlier report and to provide additional blocking efficiency data obtained by a very simple, inexpensive but efficient and reliable column chromatography method.

II. Experimental Section

The chemicals and the analytical techniques (^{1}H NMR spectroscopy and GPC) employed have been reported (1). In this research a simple but efficient gravity column chromatography method has been developed to separate the products obtained, i.e, the desired diblock and homopolymer contaminants. Thus a glass chromatography column (effective length: 51 cm, I.D.: 2.5 cm, ACE GLASS) was packed with 50g silica gel (70-230 mesh, 60 Å, ALDRICH) suspended in 150 mL n-

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pentane. A small amount (1-2g) of the diblocking reaction product was dissolved in 10 mL of a mixture of n-pentane and tetrahydrofuran (2:1 v/v) and the solution poured on top of the silica gel column. After 1 hour (to allow the absorption of the polymer on the surface of the silica gel) the dropwise addition of the first eluent (n-pentane) from a separatory funnel was started at a very slow rate (~1 mL/min). A constant eluent level (~5mL) was maintained above the silica gel. First n-pentane was used, which is a good solvent for PIB followed by THF which is a good solvent for both the PIB and PMeVE homopolymers. At least 20 fractions were taken.

III. Results and Discussion

The first part of this section concerns a replication of diblock syntheses (1) in large test tubes. The second part describes the determination of blocking efficiencies by column chromatography.

III.1 Block Copolymerizations

We demonstrated (1) that the PMeVE segment length in PIB-b-PMeVE diblock is controlled by the $TiCl_4$ concentration in the charge. Thus, five large test tubes were charged with $TMPCl/nBu_4NCl/IB$ in CH_2Cl_2/Hex solvent mixtures at -80°. At zero time the $TiCl_4$ was added to all the charges (for reagent concentrations see Table 1). After 8 min, when the conversion of IB was ~100%, the first reactor was quenched with 1 mL prechilled methanol and an appropriate amount of MeVE was added to the remaining reactors. After 10 min the polymerization in the second reactor was quenched and $TiCl_4$ stock solution was added to the rest of the reactors. This procedure, i.e, the incremental addition of $TiCl_4$, was repeated until even the last reactor was quenched. The results are collected in Table 1.

Table 1. Block copolymerization of IB and MeVE by incremental $TiCl_4$ addition

($[TMPCL]=2.7\cdot 10^{-4}$ mol, $[TiCl_4]_o=3.51\cdot 10^{-3}$ mol, $[nBu_4NCl]=1.23\cdot 10^{-3}$ mol, $[IB]=1.28\cdot 10^{-2}$ mol, in CH_2Cl_2/hex (60/40 v/v) at -80°C, volume=20 mL; after 8 min. $[MeVE]=3.1\cdot 10^{-2}$ mol added followed by the addition of $[TiCl_4]=7.28\cdot 10^{-3}$ mol every 10 mins. (see text for detailed description))

	$TiCl_4$ added 10^3 x mol	Wp g	$\overline{M}_n$ g/mole	$\overline{M}w/\overline{M}_n$	Nx10^{4}*	Theor. $\overline{M}_n$'s assuming 1:1 or 1:2 $TiCl_4$: MeVE complexes	
						1:1	1:2
1.	-	0.7527	3400	1.37	2.20	-	-
2.	-	1.0048	3600	1.42	2.79	3800	4300
3.	7.28	1.7698	6080	2.15	2.90	5400	7400
4.	2x7.28	2.5946	9100	1.76	2.85	6990	10600
5.	3x7.28	2.5402	9300	1.70	2.73	8500	13700

* $N=Wp/\overline{M}_n$

Figure 1 shows the $\overline{M}_n$ of the diblock as the function of Wp (g polymer) obtained. The molecular weight of the diblock increases upon $TiCl_4$ addition, while the number of chains remains constant and within experimental error of that of the initiator (TMPCl) in the charge. The molecular weight distribution first broadened but after the first $TiCl_4$ addition narrowed, indicating slow crossover from the living $PIB^{\oplus}$ to the $PIB\text{-}MeVE^{\oplus}$.

In agreement with earlier observations (1), the experimental $\overline{M}_n$ of the growing diblock falls in-between the $\overline{M}_n$'s calculated by assuming 1:1 or 1:2 $TiCl_4$:MeVE complexes (see Figure 2). The arrow indicates the (theoretical) molecular weight of the PIB-b-PMeVE diblock at 100% MeVE conversion.

Identical block copolymerization experiments have also been carried out in the presence of DMA. Table 2 shows the results. The molecular weight and the number of PIB chains obtained in the first phase of the block copolymer synthesis were close to the theoretical value ($N_{theor}=2.7.10^{-4}$) but increased (by ~40%) immediately upon MeVE addition. MeVE conversion and polymer composition did not change during the experiment (see Table 2); these observation are in good agreement with the proposed mechanism of MeVE polymerization in the presence of $TiCl_4$ (1). Assuming 1:1 and 1:2 $TiCl_4$:MeVE complexes, MeVE conversion is 11% and 22%; respectively. While the active polymerization charges did not exhibit discoloration, the products were UV active and the ^1H NMR spectra (not shown) revealed evidence for the presence of multiple unsaturation. Evidently, the extent of degradation by dealcoholation was reduced because of the low temperature and low polarity of the solvent used.

Table 2. Block copolymerization of IB and MeVE in presence of DMA.

([TMPCl]=$2.7\cdot10^{-4}$ mol, [$TiCl_4$]=$3.51\cdot10^{-3}$ mol, [DMA]=$2.8\cdot10^{-4}$ mol, [IB]=$1.28\cdot10^{-2}$ mol, in CH_2Cl_2/hex (60/40 v/v) at -80°C, after 15 min. [MeVE]=$3.1\cdot10^{-2}$ mol added)

	Time min	Wp g	$\overline{M}_n$ g/mole	$Mw/\overline{M}_n$	PMeVE* mole %	N** $X10^4$
1.	15	0.7053	2890	1.45	-	2.44
2.	25	1.1061	3150	1.40	22	3.51
3.	35	1.1005	3310	1.36	-	3.32
4.	45	1.1441	3400	1.42	-	3.36
5.	75	1.1919	3200	1.62	20	3.62
6.	115	1.1125	4000	1.44	21	2.78

*by ^1H NMR spectroscopy

**$N=Wp/\overline{M}_n$

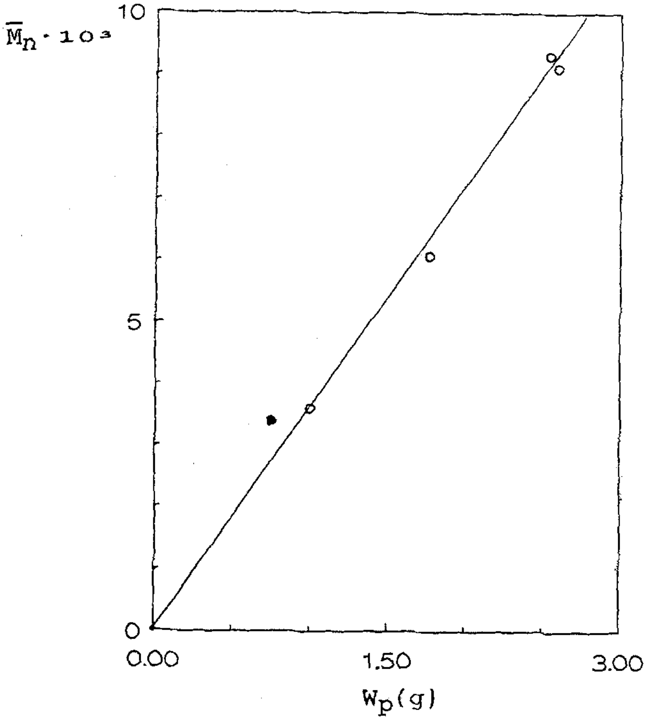
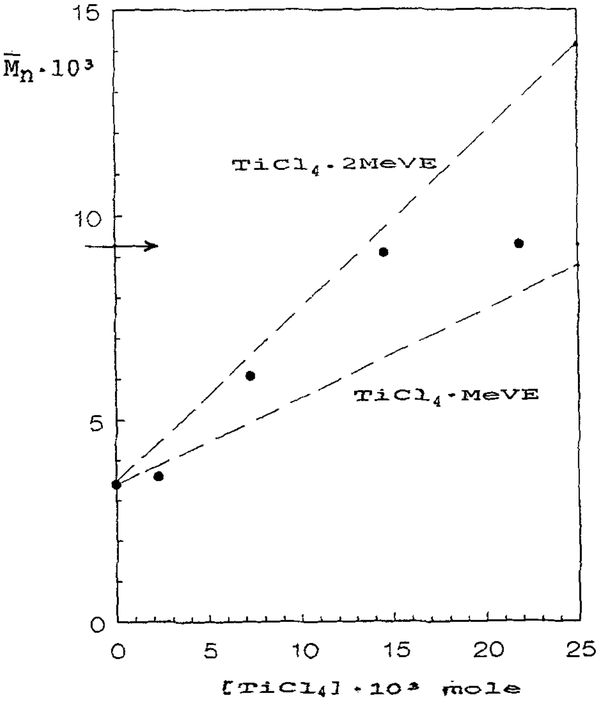


Figure 1. $\overline{M}_n$ versus W_p (weight) of block copolymer) plot for block copolymerization of IB and MeVE. For conditions see Table 1. ● PIB, ○ PIB-*b*-PMeVE

Figure 2. $\overline{M}_n$ versus $[TiCl_4]$ added for the block copolymerization of IB and PMeVE



III.2 Column Chromatography

The final products obtained in each series (sample 5 of Table 1, and sample 6 of Table 2) were examined by column chromatography. The data are collected in Tables 3 and 4. The eight columns show, respectively, the eluent used, the volume of eluent, the weight of the fraction, the weight percent of the fraction, the cumulative weight fraction, the M_n of the fraction, the PMeVE content of the fraction, and the number of diblock molecules in the fraction. Figures 3 and 4 show the wt% of the fraction versus eluent volume (mL). The product obtained in presence of nBu_4NCl is essentially pure diblock (>96w% PIB-b-PMeVE) while that prepared in presence of DMA is mainly (~72w%) PIB plus ~21w% PIB-b-PMeVE and ~5w% PMeVE. According to composition data obtained with DMA shown in Table 4 (fractions 3,4,6 and 9,10,11) the crossover preferably involves low M_n PIB$^{\oplus}$ while the longer chains remain largely unblocked.

This large difference in blocking efficiencies, i.e, B_{eff}>95% with nBu_4NCl and B_{eff} ~20% with DMA, is most likely due to different chain-end structures. In the presence of nBu_4NCl the growing site is arguably a polarized covalent bond $(\sim\overset{\delta\oplus}{C}---\overset{\delta\ominus}{Cl}.TiCl_4)$ while in the presence of an electron donor (DMA) the growing end is more complex (2).

Table 3. Column chromatography of the diblock obtained in the presence of nBu_4NCl (sample 5 of Table 1)
Wp of sample loaded = 2.3058 g

	Eluent	V_{el} mL	Wpi g	W_i %	ΣW_i %	M_n g/mole	PMeVE mol%	N X10^6
1.	pentane	30	0.0020	0.08	0.08	-	-	-
2.	pentane	60	0.0025	0.11	0.19	-	-	-
3.	pentane	80	0.0028	0.12	0.31	-	-	-
4.	pentane	100	0.0137	0.59	0.90	-	-	-
5.	pentane	120	0.0263	1.14	2.04	2500	0	10.5
6.	pentane	140	0.0219	0.95	2.99	2950	0	7.4
7.	pentane	160	0.0053	0.23	3.22	-	-	-
8.	pentane	180	0.0024	0.10	3.32	-	-	-
9.	pentane	200	0.0021	0.09	3.41	-	-	-
10.	pentane	220	0.0021	0.09	3.50	-	-	-
11.	pentane	240	0.0013	0.05	3.55	-	-	-
12.	THF	260	0.1414	6.16	9.71	-	-	-
13.	THF	280	0.1919	8.32	18.03	6900	50	27.4
14.	THF	300	0.4363	19.01	37.04	8600	70	50.5
15.	THF	320	0.4138	18.03	55.07	10150	72	40.7
16.	THF	340	0.2771	12.07	67.14	10720	-	25.8
17.	THF	360	0.1941	8.45	75.59	10300	-	18.8
18.	THF	380	0.1748	7.62	83.21	10640	-	16.4
19.	THF	400	0.1446	6.30	89.51	10140	78	14.2
20.	THF	420	0.0857	3.73	93.24	10340	-	8.28
21.	THF	440	0.0632	2.75	95.99	-	-	-
22.	THF	640	0.0906	3.94	99.44	-	81	-

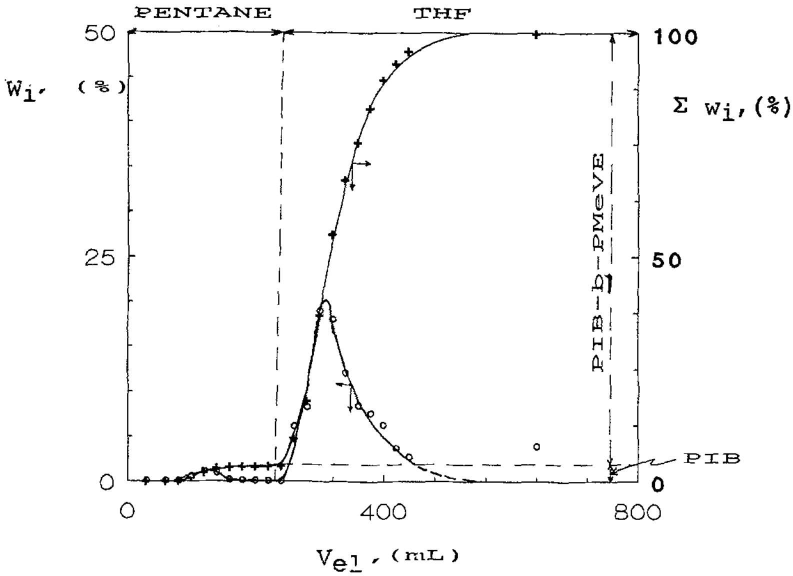


Figure 3. Column chromatography of the polymer obtained in the presence of nBu_4NCl (sample 5 of Table 1). For conditions see Experimental

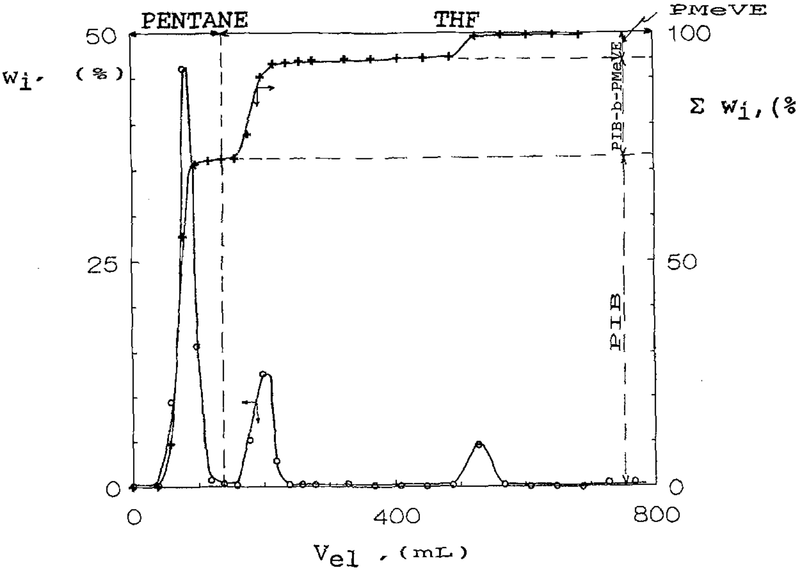


Figure 4. Column chromatography of the polymer obtained in the presence of DMA (sample 6 of Table 2)

Table 4. Column chromatography of the diblock obtained in the presence of DMA (sample 6 of Table 2)
Wp of sample loaded = 1.0854 g

	Eluent	V_{el} mL	Wpi g	W_i %	ΣW_i %	$\overline{M}_n$ g/mole	PMeVE mol%	N $x10^6$
1.	pentane	20	0.0004	0.04	0.04	-	-	-
2.	pentane	38	0.0014	0.15	0.19	-	-	-
3.	pentane	58	0.0862	9.48	9.67	5080	0	1.7
4.	pentane	78	0.4202	46.13	55.80	4000	0	10.5
5.	pentane	98	0.1436	15.76	71.56	3600	0	3.98
6.	pentane	118	0.0065	0.71	72.27	-	-	-
7.	THF	138	0.0031	0.34	72.61	-	-	-
8.	THF	158	0.0014	0.15	72.76	-	-	-
9.	THF	178	0.0470	5.16	77.92	5960	83	0.79
10.	THF	198	0.1149	12.61	90.53	4920	95	2.3
11.	THF	218	0.0263	2.88	93.41	4320	97	0.61
12.	THF	238	0.0024	0.26	93.67	-	-	-
13.	THF	258	0.0021	0.23	93.90	-	-	-
14.	THF	278	0.0019	0.21	94.11	-	-	-
15.	THF	328	0.0028	0.30	94.41	-	-	-
16.	THF	368	0.0014	0.15	94.56	-	-	-
17.	THF	408	0.0009	0.10	94.66	-	-	-
18.	THF	448	0.0006	0.06	94.72	-	-	-
19.	THF	488	0.0014	0.15	94.87	-	-	-
20.	THF	528	0.0425	4.66	99.53	4200	100	1.0
21.	THF	568	0.0021	0.23	99.76	-	-	-
22.	THF	608	0.0006	0.06	99.82	-	-	-
23.	THF	648	0.0001	0.01	99.83	-	-	-
24.	THF	688	0.0000	0.00	99.83	-	-	-
25.	THF	728	0.0004	0.44	100.27	-	-	-
26.	THF	768	0.0004	0.44	100.71	-	-	-

IV. Conclusion

In the presence of a common ion salt (e.g., nBu_4NCl), the living $PIB^{\oplus}$ upon the addition of MeVE readily yields PIB-b-PMeVE diblocks by sequential monomer addition and with high blocking efficiencies. In contrast, electron donor (e.g., DMA) mediated living IB polymerization gives relatively low blocking efficiencies. In the latter system the number of chains increases immediately upon MeVE introduction into a living $PIB^{\oplus}$ charge indicating the onset of chain transfer. The large difference in blocking efficiencies suggests that the structure of the living ends in common salts and electron donor mediated $LC^{\oplus}$ Pzn's are different.

Acknowledgments

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