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SYNTHESIS OF POLY(N-VINYLCARBAZOLE-b-ISOBUTYLVINYLETHER)

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ABSTRACT

Blockcopolymers consisting of N-vinylcarbazole (NVC) and isobutylvinylether (IBVE) were synthesized by sequential monomer addition. It is essential to start the synthesis with the NVC-segment and to initiate the polymerization by 1-iodo-1-(2-methylpropyloxy)ethane. The blockcopolymerization of IBVE proceeds only in the presence of an activator, such as $(n\text{-}Bu)_4NClO_4$. The blockcopolymers were characterized by GPC, ^1H NMR, elemental analysis and DSC.

INTRODUCTION

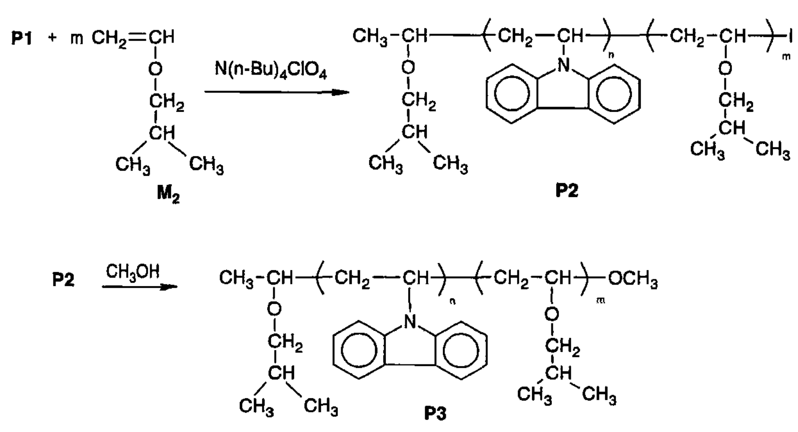
From earlier studies we know that 1-iodo-1-(2-methylpropyloxy)ethane is a suitable initiator for the polymerization of NVC$^{1)}$. We were able to show that poly(N-vinylcarbazole) (poly(NVC)) can be obtained with a molar mass which is controlled by [M] : [I], and that molar mass distribution is narrow. Furthermore, incremental monomer addition experiments indicated that all chain ends could be reactivated again for a further polymerization.

These observations encouraged us to look for conditions which allow blockcopolymerization.

It was also known that the polymerization of isobutylvinylether by 1-iodo-1-(2-methylpropyloxy)ethane **1** alone failed. The addition of an activator ($(n\text{-Bu})_4NClO_4$) is needed[2]. The polymerization of NVC in the presence of both 1-iodo-1-(2-methylpropyloxy)ethane and $(n\text{-Bu})_4NClO_4$ is not living. Consequently, it was essential to start the synthesis of the blockcopolymer with the NVC-segment initiated by **1** alone.

RESULTS AND DISCUSSION

Poly(N-vinylcarbazole-b-isobutylvinylether) (poly(NVC-b-IBVE)) was synthesized according to the following scheme:



Polymerization of NVC was initiated with 1-iodo-1-(2-methylpropyloxy)ethane (**1**) at -50°C - conversion was followed by GC with xylene as internal standard.

After complete conversion of M_1 the temperature was raised to -20°C and then the IBVE (M_2) was added. However, no polymerization was observed before the activator $(n\text{-}Bu)_4NClO_4$ was added, meaning that **P1** alone was not able to start a IBVE polymerization.

As one can see from TABLE 1, both monomers were converted almost completely. Furthermore, in all cases monomodal GPC curves were received, which we consider a strong indication that blockcopolymers of NVC and IBVE are formed.

The calculated and the observed molar masses are similar, indicating that both monomers react in a living manner. We have been surprised to see that calibration of the GPC with polystyrene works perfect for poly(NVC-b-IBVE). This is supported by independent tests by vapor pressure osmometry (exp. 1, exp. 6) (TABLE 2).

The composition of blockcopolymers was determined by proton NMR and elemental analysis. A typical ^1H NMR-spectrum of a poly(NVC-b-IBVE) is shown in FIG. 1.

Since the spectrum contains independent signals belonging to each of the units: area between 8 and 4,5 ppm corresponds with 8 protons of NVC (a) signal at 0,9 ppm corresponds with 6 protons of IBVE (h), it is possible to calculate the composition of the blockcopolymer on the basis of the following simple relation:

$$X_{NVC} = \frac{I_{NVC}}{I_{NVC} + I_{IBVE}}$$

I_{NVC} = a/8; a = area between 8 and 4,5 ppm

I_{IBVE} = h/6; h = area of signal at 0,9 ppm

TABLE 1:
Blockcopolymers for NVC and IBVE
Initiator: 1-iodo-1-(2-methylpropyloxy)ethane (**1**)
for NVC, and **1**/$(n\text{-}Bu)_4NClO_4$ (**2**) for IBVE
T = -50°C for NVC, T = -20°C for IBVE

Exp	[NVC] mol l^{-1}	[**1**] mol l^{-1}	$C^{a)}$ %	[IBVE] mol l^{-1}	[**1**] mol l^{-1}	[**2**] mol l^{-1}	$C^{b)}$ %
1	0,15	0,01	98,6	0,13	0,009	0,0095	90,6
2	0,17	0,01	95,3	0,13	0,009	0,0083	85,2
3	0,20	0,01	96,7	0,13	0,009	0,0091	91,7
4	0,15	0,01	96,3	0,28	0,009	0,0090	91,7
5	0,15	0,01	97,8	0,23	0,009	0,0090	94,3
6	0,14	0,0035	$65,5^{c)}$	0,13	0,003	0,0030	37,4

a) Conversion of NVC after 3 hrs;
b) Conversion of IBVE after 1,5 hrs
c) A conversion of 93.6% was reached after raising the temperature to -20°C.

$X_{NVC} = n/[n + (m+1)]$; n = number of repeating units of NVC, m = number of repeating units of IBVE (+1, due to the initiator unit).

The composition of the blockcopolymer is also calculated on the basis of the elemental analysis. The results of proton NMR and elemental analysis are compared with calculated values based on the conversion data in TABLE 3.

THERMAL PROPERTIES OF POLY(NVC-b-IBVE)

It is known that the glass transition temperature of both homopolymer PNVC and PIBVE are very different: Tg

TABLE 2:
Molar masses of the poly(NVC-b-IBVE)

Exp.	M_n(GPC)	M_n(VPO)	M_n(calc)$^{a)}$	M_w/M_n
1	4390	3900	4340	1,34
2	5200	-	4650	1,40
3	5420	-	5320	1,46
4	5620	-	5890	1,45
5	5880	-	5440	1,45
6	8810	8200	9350	1,50

a) calc. from $M_n = [M_1]/[I_1] \cdot C_1^* \cdot M_{M1}$
$+ [M_2]/[I_2] \cdot C_2^* \cdot M_{M2} + M_{head} + M_{end}$

* C = conversion

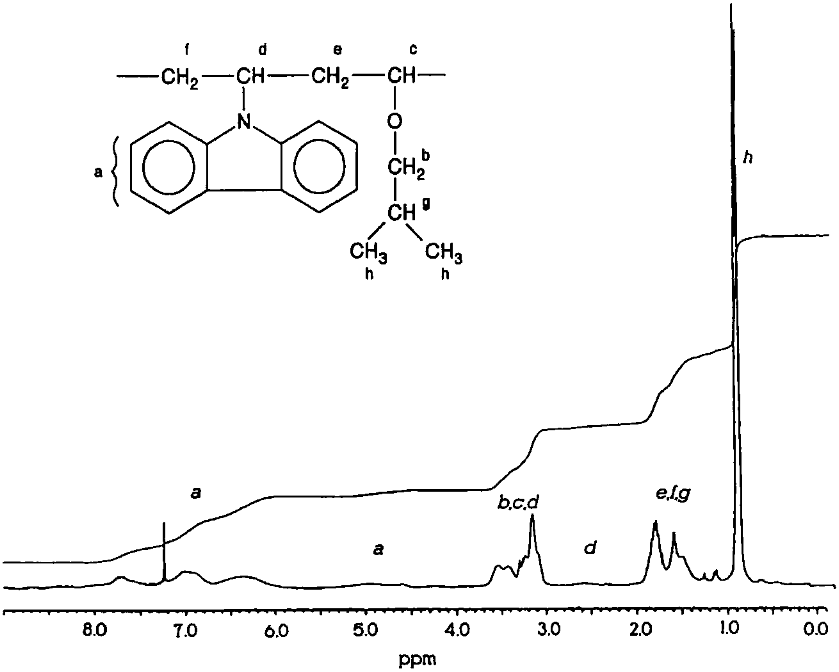


Fig.1: ^{1}H NMR of poly(NVP-co-IBVE) in $CDCl_3$.

TABLE 3:

Composition of the blockcopolymers in mol%

Exp.	NVC			IBVE		
	calc.[a]	^{1}H NMR	EA[c]	calc.[b]	^{1}H NMR	EA[c]
1	51,5	54,9	54,4	48,5	45,1	45,6
2	56,1	58,5	59,5	43,9	41,5	40,5
3	58,5	68,4	67,7	41,5	31,6	32,3
4	33,7	32,1	27,5	66,3	67,9	72,5
5	37,4	40,0	36,7	62,6	60,0	63,3
6	69,9	74,4	73,1	30,1	25,6	26,9

a) based on complete conversion of NVC

b) based on the conversion, given in table 1. The number of repeating units is given by:
n = [IBVE]/[I] · C + 1 (because of the initiator unit)

c) based on the elemental analysis

(PNVC): 205°C[3,4], Tg (PIBVE) = -20°C[4]. It was of interest whether poly(NVC-b-IBVE) would show a Tg depending on its composition or two separated Tg's. The result is shown in FIG. 2:

Since DSC curves of the mixture of the two homopolymers and of the block copolymers are almost identical, one can conclude that the segments of the blockcopolymer have a strong tendency for phase separation.

Both Tg-values are very close to those of the homopolymers.

EXPERIMENTAL PART

INSTRUMENTS

IR: Digilab FTS-40 (FT-IR); ^{1}H NMR: Bruker AC 250 (250 MHz); ^{13}C NMR: Bruker AC 250 (62,5 MHz); GPC: Waters 510,

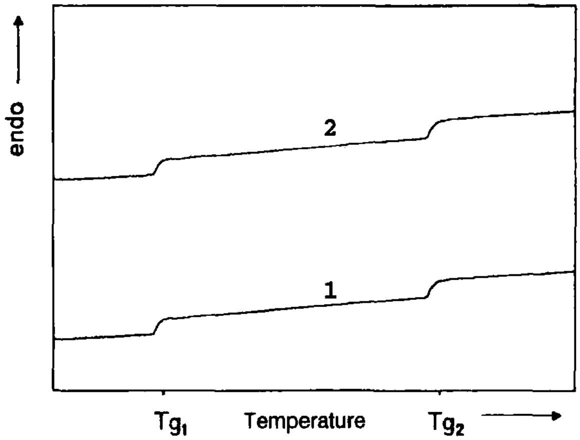


FIG. 2: DSC of poly(NVC-b-IBVE) (**2**) and a mixture of PNVC and PIBVE (**1**)

RI 590, eluent: THF; DSC: Perkin Elmer DSC7; GC: Varian GC 3700, column. CP Sil 5CB; Elemental analysis: Ilse Beetz, Kronach; Cryostate: Lauda UK 8 DW.

CHEMICALS

CH_2Cl_2 was dried over CaH_2. Xylene was dried with sodium. N-vinylcarbazole (Fluka) was recrystallized from n-hexane. Isobutylvinylether (Fluka) was refluxed over CaH_2 and it was freshly destilled before use.

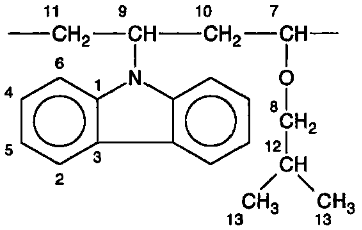
$(n\text{-}Bu)_4NClO_4$ (Fluka) was dried for 24 hrs. under high vacuum conditions and then it was stored under argon. 1-iodo-1(2-methylpropyloxy)ethane (**1**) was synthesized as described in the literature[2].

Polymerization

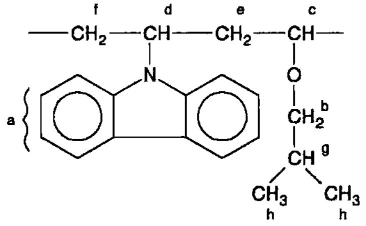
The polymerization was started with NVC/**1** (values see TABLE 1) in CH_2Cl_2 at -50°C in the presence of xylene as internal standard (for quant. determination of conversion by GC). After complete conversion of NVC a

certain amount of IBVE (see TABLE 1) was added. The system was heated to -20°C before the polymerization was started by addition of the activator $(n\text{-}Bu)_4NClO_4$. The progress of polymerization was followed by GC.
After ~90% conversion of IBVE the polymerization was quenched with methanol/aqu. NH_3, the precipitated polymer was collected by filtration, dried and characterized.

Characterization
^{1}H NMR ($CDCl_3$) δ (ppm): 5,8-8,0 (H^a), 4,5-5,2 (H^a), 3,0-3,9 (H^b, H^c, H^d), 2,3-2,8 (H^d), 1,0-2,0 (H^e, H^f, H^g), 0,9 (H^h)



^{13}C NMR ($CDCl_3$) δ (ppm): 140,4 and 137,9 (C^1), 125 (C^2), 123,8 and 122,2 (C^3), 120,3 (C^4), 119,6 (C^5), 111,5 and 108,2 (C^6), 75,6 (C^7), 73,6 (C^8), 48,5 (C^9), 42-37 (C^{10}), 37-33 (C^{11}), 28,8 (C^{12}), 19,6 (C^{13})



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