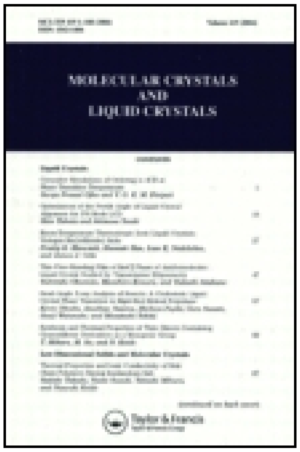

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Laterally Aromatic Branched Two-Ring Mesogens Connected to Polysiloxane Backbone

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LATERALLY AROMATIC BRANCHED TWO-RING MESOGENS CONNECTED TO POLYSILOXANE BACKBONE

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Abstract Surprisingly, two-ring mesogens with a phenyl ring containing lateral segment can show liquid-crystalline behaviour. Linking to a polysiloxane backbone can be realized via three different para positions of the mesogens. Polymorphism and mesophase stabilization depend strongly on the position and type of substituents as well as on the length and position of the spacer.

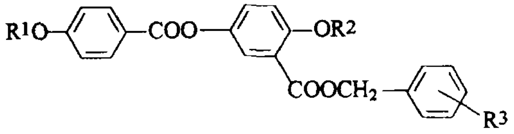
Keywords: laterally branched mesogens, polysiloxanes

INTRODUCTION

A lot of liquid crystalline side group polymers containing rod-like or disc-like mesogens are known[1, 2]. For some years, there are intensive efforts to find molecules which have deviating structures, which, nevertheless, are able to form mesophases and to link such nonconventional mesogens to a polymer backbone. E.g., Lin et al. [3] and Cabrera et al. [4] described polymers with mesogens of half-phasmidic structures. Achard et al. [5] reported about polysiloxanes with forked mesogens. Heinemann et al.[6] and Hohmuth et al.[7] synthesized polysiloxanes bearing swallow-tailed mesogens. In all of these cases the wedge-shaped mesogens were attached terminally to the polymer backbone.

Some years ago, Weissflog et al.[8] were succesfully to synthesize three-ring mesogens with lateral aromatic branches, which are able to form mesophases despite of their unusual molecular shape. Recently, we reported on the first two-ring mesogens having a substituted phenyl ring within the lateral segment[9].

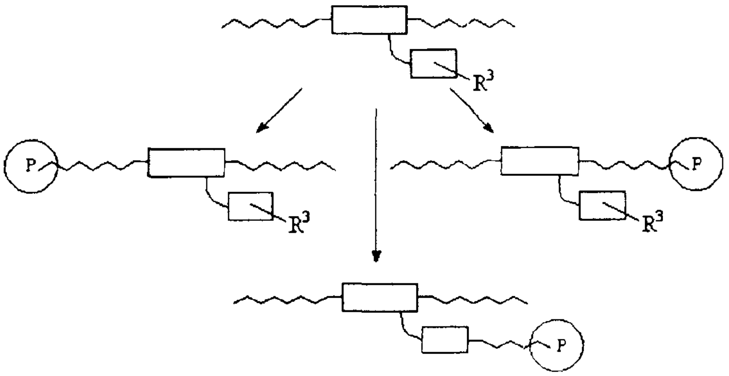
In this paper we would like to present a family of side group polysiloxanes with laterally branched two-ring mesogens of the following formula:



$R1, R2 = -C_mH_{2m+1}; -(CH_2)_{n-2}-CH=CH_2$

$R3 = -CN, -O(CH_2)_{n-2}-CH=CH_2$

By substitution the molecules into the positions R^1, R^2 or R^3 by alkenyl groups three possibilities result to link such new mesogens via a para-position to a polysiloxane chain.



The position and length of the spacer as well as the kind and position of R^3 (H, CN, alkenyloxy) should be of influence on the mesophase behaviour of the polysiloxanes.

SYNTHESIS

The synthesis of the alkene precursors 3 (R^3: H, CN) was realized according to a reaction pathway described earlier[9], sketched in figure 1.

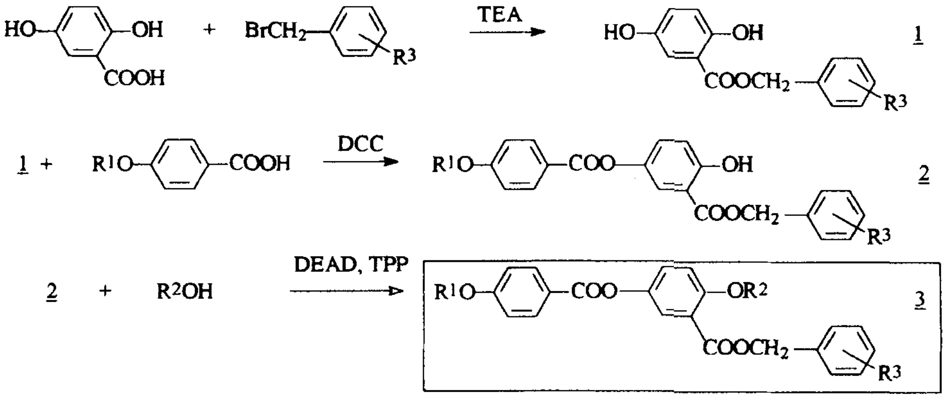


FIGURE 1 Synthetic pathway to obtain mesogens 3.

To prepare the 3-cyanosubstituted substance 1b and the unsubstituted benzyl derivative 1d esterification was succesfully using a heterogenous solid state reaction in analogy to the method given by Barry et al.[10]

Figure 2 shows the reaction path to synthesize the monomeric compounds 5 bearing an unsaturated chain at the lateral phenyl ring.

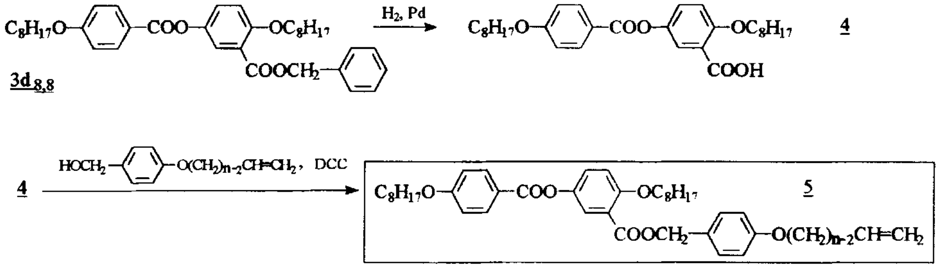


FIGURE 2 Synthetic pathway to obtain mesogens 5.

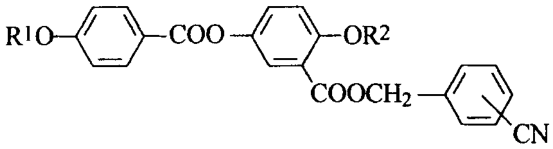
By hydrogenolytic cleavage of the benzylester $3d_{8,8}$ using Pd on carbon the benzoic acid 4, exhibiting liquid crystalline properties itself (Cr 81 (N 66,5) I) could be obtained. Esterification of 4 with 4-ω-alkenyloxybenzylic alcohols by means of DCC/DMAP yielded the mesogens 5. By hydrosilylation reaction of the low-molecular mesogens 3 and 5 to polymethylhydrogensiloxane (P_n = 35) using hexachloroplatinic acid dihydrate[11] in isopropanol as catalyst the polymers P3 and P5 were produced.

RESULTS

The melting points and mesophase behaviour of the alkene precursors 3a-3c and the corresponding polymers P3a-P3c can be compared in Table I. The liquid crystalline properties and phases were characterized by optical microscopy, DSC and X-ray diffraction, if possible.

Only the low molecular substances bearing the cyano group in para-position of the lateral phenyl ring show liquid crystalline phases. For the polymers alteration of the cyano group from the ortho via the meta to the para position leads to a pronounced formation of smectic phases and increasing of the mesophase stability. Generally, lengthening of the spacers leads to an increasing of the clearing temperatures and to a dominance of smectic phases.

Table I[a)]: Transition temperatures (Grad C) of the low molecular mesogens 3 and corresponding polymers P3.



CN in: 2-position: 3a
3-position: 3b
4-position: 3c

alkene precursors 3							polysiloxanes P3					
no.	R^1	R^2	cr	S_A	N	I	no.	T_g	S	N	I	$\Delta T_{(lc-I)}$[b)]
$3a_{3,8}$	**C_3H_5**	C_8H_{17}	. 92	-	-	.	$P3a_{3,8}$	c)	-	-	.	-
$3a_{6,8}$	**C_6H_{11}**	C_8H_{17}	. 45	-	-	.	$P3a_{6,8}$	. 8	-	. 62	.	-
$3a_{11,8}$	**$C_{11}H_{21}$**	C_8H_{17}	. 47	-	-	.	$P3a_{11,8}$	c)	S_X[d)] 64	-	.	-
$3a_{8,3}$	C_8H_{17}	**C_3H_5**	. 68	-	-	.	$P3a_{8,3}$	c)	-	-	.	-
$3a_{8,6}$	C_8H_{17}	**C_6H_{11}**	. 42	-	-	.	$P3a_{8,6}$	c)	-	. 36	.	-
$3a_{8,11}$	C_8H_{17}	**$C_{11}H_{21}$**	. 87	-	-	.	$P3a_{8,11}$	c)	. 70	-	.	-
$3b_{3,8}$	**C_3H_5**	C_8H_{17}	. 78	-	-	.	$P3b_{3,8}$	c) 14	-	. 52	.	-
$3b_{6,8}$	**C_6H_{11}**	C_8H_{17}	. 41	-	-	.	$P3b_{6,8}$	. 8	S_X[d)] 48	-	.	-
$3b_{11,8}$	**$C_{11}H_{21}$**	C_8H_{17}	. 43	-	-	.	$P3b_{11,8}$	. 7	S_A 76	-	.	-
$3b_{8,3}$	C_8H_{17}	**C_3H_5**	. 53	-	-	.	$P3b_{8,3}$	c)	-	-	.	-
$3b_{8,6}$	C_8H_{17}	**C_6H_{11}**	. 37	-	-	.	$P3b_{8,6}$	c)	-	. 45	.	-
$3b_{8,11}$	C_8H_{17}	**$C_{11}H_{21}$**	. 37	-	-	.	$P3b_{8,11}$	. 7	S_A 80	-	.	-
$3c_{3,8}$	**C_3H_5**	C_8H_{17}	. 83	-	(. 48)	.	$P3c_{3,8}$	. 24	-	. 95	.	47
$3c_{6,8}$	**C_6H_{11}**	C_8H_{17}	. 68	(. 45	. 49)	.	$P3c_{6,8}$	. 21	S_A 102	-	.	53
$3c_{11,8}$	**$C_{11}H_{21}$**	C_8H_{17}	. 56	. 62	-	.	$P3c_{11,8}$	. 15	S_A 124	-	.	62
$3c_{8,3}$	C_8H_{17}	**C_3H_5**	. 76	-	-	.	$P3c_{8,3}$	c)	-	-	.	-
$3c_{8,6}$	C_8H_{17}	**C_6H_{11}**	. 60	(. 32	. 41)	.	$P3c_{8,6}$	. 48	S_C 55	. 73	.	32
$3c_{8,11}$	C_8H_{17}	**$C_{11}H_{21}$**	. 54	. 69	-	.	$P3c_{8,11}$	. 15	S_A 127	-	.	58

[a)] In the table the unsaturated alkyl chains are fat printed, the substances are labelled $3a\text{-}c_{n,m}$ for n = number of carbon atoms in R^1 and m = number of carbon atoms in R^2

[b)] $\Delta T_{(lc-I)} = T_{(lc-I)}$ polymer - $T_{(lc-I)}$ monomer

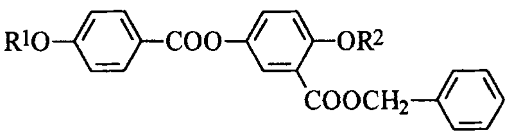
[c)] could not be detected above -10°C

[d)] S_X not classified smectic phase, it could be a smectic A or smectic C phase.

Unusual relationships can be observed for polymers with the shortest spacerlength of n=3. None of the polymers show mesophases, if the spacer is connencted in 2-position (R^1), that means at the broader part of the wedge-shape molecules. However, linking the mesogens in 5-position can produce polysiloxanes with liquid crystalline phases. Steric hindrance could be the reason for this different behaviour.

In order to answer the question, how far polar groups (cyano- or nitro group) situated at the lateral segment of the mesogens under discussion are necessary for the formation of mesophases the appropriate laterally unsubstituted substances 3d and P3d were synthesized. The phase transition temperatures of 3d and the corresponding polysiloxanes P3d are listed in Table II.

TABLE II[a]: Phase behaviour of benzyl esters 3d and the polymers P3d.



3d

		alkene precursors 3d				polysiloxanes P3d			
no.	R^1	R^2	cr	N	I	no.	T_g	S_A	I	$\Delta T_{(lc\text{-}I)}$[b]
$3d_{8,3}$	C_8H_{17}	**C_3H_5**	. 66	-	.	$P3d_{8,3}$	[c]	-	.	-
$3d_{8,6}$	C_8H_{17}	**C_6H_{11}**	. 51	[d]	.	$P3d_{8,6}$	[c]	. 64	.	-
$3d_{8,11}$	C_8H_{17}	**$C_{11}H_{21}$**	. 55	(. 26,5)	.	$P3d_{8,11}$	[c]	. 78	.	51,5

[a], [b], [c] see TABLE I

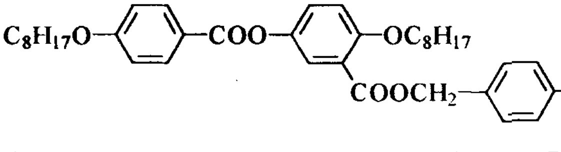
[d] mesophases could not be observed above 19,0 °C

Only the alkene precursor $3d_{8,11}$ having the longest terminal chains shows a nematic phase of low thermal stability. But by linking the mesogens 3d with a spacerlength n=6 ($P3d_{8,6}$) or n=11 ($P3d_{8,11}$, $\Delta T_{lc\text{-}I}$ = 51,5 K) to the polysiloxane backbone it is possible to obtain polymers, which show a smectic A Phase with higher stability.

By installing the spacer in the lateral position R^3 a third possibility to connect the mesogens to the polymer backbone is opened as shown in Table III.

All the monomers bearing an alkenyl chain in para-position of the lateral aromatic ring show monotropic nematic phases. Therefore, the existence of mesophases is not bound with polar groups, like cyano or nitro, at the lateral segment. But the substituents in R^3 determine the type of phases. Whereas substances with a nitro group in this position only show smectic A phases as described recently[9], the cyano substituted compounds can exhibit nematic and smectic A phases. As seen in Table III, aliphatic chains in this position cause nematic phases.

TABLE III[a]: Phase transition behaviour of the monomers 5 laterally connected to the backbone in the polymers P5.



5

		alkene precursors 5					polysiloxanes P5								
no.	R^3	cr		N		I	no.	T_g		S_X[d]		N		I	$\Delta T_{(Ic-I)}$[b]
5_3	**OC_3H_5**	.	47	(.	44)	.	$P5_3$	-		-		.	48	.	4
5_6	**OC_6H_{11}**	.	69	(.	44)	.	$P5_6$	.	39	.	52	.	63	.	19
5_{11}	**$OC_{11}H_{21}$**	.	61	(.	46)	.	$P5_{11}$	-		-		.	76	.	30

[a] In the table the unsaturated alkyl chains in R^3 are fat printed, the substances are labelled 5_n for n = number of carbon atoms in R^3.
[b], [d] see TABLE I

Linking these unsaturated compounds 5 to polysiloxane yields polymers having a molecular architecture unknown yet. Mesophase stabilization induced by the polyaddition strongly depends on the spacer length. The clearing temperatures of the monomer 5_3 as well as polymer $P5_3$ having three methylene units in the spacer are nearly the same. Stabilization by 30 K can be observed for the mesogen with the longest spacer (n=11).

EXPERIMENTALS

2-Cyanobenzyl 2,5-dihydroxybenzoate (1a) and 4-Cyanobenzyl 2,5-dihydroxybenzoate (1c):

A solution of 28.9 g (0.1 mol) cyanobenzylbromide in 50 ml dry acetone is added slowly to 15.4 g (0.1 mol) 2,5-dihydroxybenzoic acid, 14.2g (0.1 mol) triethylamine and catalytic amounts of sodium iodide in 250 ml dry acetone during stirring. After refluxing for 4 hours the mixture is put into 600 ml water, the precipitated product is filtered of and recrystallized from ethanol. 1a: m.p. 142 °C, yield 80 %; 1c: m.p. 178 °C, yield 76 %

1a: ^{1}H-NMR (80 MHz, $CDCl_3$): δ= 4,75 (s, 1H, HO-), 5,6 (s, 2H, COO-CH_2-Ar), 6,9-7,8 (m, 7H, Ar), 10,1 (s, 1H, -OH)

3-Cyanobenzyl 2,5-dihydroxybenzoate (1b) and benzyl 2,5-dihydroxybenzoate (1d):
16 g (0.06 mol) potassium 2,5-dihydroxybenzoate (prepared by dissolving of 2,5-dihydroxybenzoic acid in the stochiometric amount of potassium hydroxide solution, evaporing the water and drying over phosphorus pentoxide), 0.06 mol benzyl bromide and 2.9 g (0.009 mol) tetrabutylammonium bromide are mixed and allowed to stand at room temperature for 2 weeks. After this time the solid mixture is solved in 100 ml aceton, stirred for 2 hours under refluxing and after cooling it is putted into 300 ml water. The precipitated ester is filtered of and recrystallized. 1b: m.p. 160 °C, yield 93 % (recrystallized from ethanol); 1d: m.p. 100 °C, yield 75 % (recrystallized from heptan/toluol (6:1)

1d: ^{1}H-NMR (80 MHz, $CDCl_3$): δ = 4,5 (s, 1H, HO-), 5,4 (s, 2H, COO-CH_2-Ar), 6,8-7,7 (m, 8H, Ar), 10,3 (s, 1H, -OH)

(Cyano)benzyl 2-hydroxy-5-(4-n-alkyloxy (or alkenyloxy) benzoyloxy)benzoates (2a-c):
A mixture of 0.27g (0.01 mol) 1, 0.01 mol 4-n-alkyloxy (or alkenyloxy) benzoic acid, 2.47 g (0.012 mol) N,N'-dicyclohexylcarbodiimide (DCC) and catalytic amounts of 4-N,N-dimethylaminopyridine (DMAP) in 100 ml dry methylene chloride is stirred for 48 hours. After filtration of the precipitated urea through a short column of silicagel the solution is washed with water, sodium hydrogencarbonate (5% solution) and again with water. Then, the organic phase is dried on sodium sulphate and the solvent is evaporated. Recrystallization from ethanol yields the pure product. Yields: 56-82%

no.	R^1	m.p. (°C)	no.	R^1	m.p. (°C)	no.	R^1	m.p. (°C)
$2a_3$	C_3H_5	138	$2b_6$	C_6H_{11}	87	$2c_6$	C_6H_{11}	91
$2a_6$	C_6H_{11}	107	$2b_8$	C_8H_{17}	62	$2c_8$	C_8H_{17}	94
$2a_8$	C_8H_{17}	102	$2b_{11}$	$C_{11}H_{21}$	65	$2c_{11}$	$C_{11}H_{21}$	66
$2a_{11}$	$C_{11}H_{21}$	93	$2c_3$	C_3H_5	114	$2d_8$	C_8H_{17}	56
$2b_3$	C_3H_5	111						

$2a_3$: ^{1}H-NMR (500MHz, $CDCl_3$): δ = 4,59-4,63 (d, 2H, =CH-CH_2-O), 5,29-5,47 (m, 2H, CH_2=CH-CH_2-), 5,56 (s, 2H, COO-CH_2-Ar), 6,01-6,09 (m, 1H, CH_2=CH-CH_2-), 6,93-8,12 (several m, 11H, Ar), 10,50 (s, 1H, -OH)

(Cyano)benzyl 2-n-alkyloxy (or alkenyloxy) -5-(4-n-alkyloxy (or alkenyloxy) benzoyloxy) benzoates (3):

To a mixture of 0.004 mol 2, 0.006 mol n-alkanol and 1.95 g (0.0075 mol) triphenylphosphine in 60 ml dry diethylether/aceton (1:1), 1.1 ml (0.75 mol) diethylazoxydicarboxylate were droped at 0°C under nitrogen. After stirring at room temperature over night the reaction mixture is washed with water, dried on sodium sulphate and the solvent is evaporated. The raw products are purified by recrystallization more than one from ethanol. Yields: 52-84 %

3a$_{3,8}$: ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0,85-0,88 (m, 3H, $C\underline{H}_3$), 1,20-1,30 (m, 8H, $(CH_2)_4$-), 1,36-1,42 (m, 2H, $C\underline{H}_2$-$(CH_2)_2$-O-), 1,74-1,80 (m, 2H, CH_2-$C\underline{H}_2$-CH_2-O-), 4,01-4,03 (t, 2H, -O-$C\underline{H}_2$-CH_2-), 4,60-4,62 (d, 2H, CH_2=CH-$C\underline{H}_2$-O), 5,30-5,32 (d, 1H, $C\underline{H}_2$=CH-), 5,40-5,44 (d, 1H, $C\underline{H}_2$=CH-), 5,51 (s, 2H, COO-$C\underline{H}_2$-Ar), 6,00-6,08 (m, 1H, CH_2=C$\underline{H}$-CH_2-), 6,95-8,12 (several m, 11H, Ar)

2-n-Octyloxy-5-(4-n-octyloxybenzoyloxy)benzoic acid (4):

6,8 mmol (4,0 g) 3d$_{8,8}$, 0,68 mmol (0,4 g) 10 % Pd on carbon in 100 ml THF and 10 ml acetic acid are shaken in a hydrogenation investment at normal pressure. The end of the reaction is detected by tlc (eluent ethylacetate). After the reaction is finished, the catalyst is filtered off, the solvent is evaporated and the product is recrystallized from ethanol.

m.p. (°C): Cr 81 (N 66,5) I , yield: 86%

4: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 0,84-0,90 (m, 6H, 2x $C\underline{H}_3$), 1,27-1,54 (m, 20H, 2x $(CH_2)_5$), 1,73-1,98 (m, 4H, 2x CH_2-$C\underline{H}_2$-CH_2-O-), 4,02-4,05 (t, 2H, -O-$C\underline{H}_2$-CH_2-), 4,22-4,28 (t, 2H, 2x -O-$C\underline{H}_2$-CH_2-), 6,91-8,13 (several m, 7H, Ar), 11,00 (s, 1H, COO$\underline{H}$)

4-n-ω-Alkenyloxybenzoyloxy 2-n-octyloxy-5-(4-n-octyloxybenzoyloxy)benzoates (5):

A mixture of 2.5g (5 mmol) of 4, 5 mmol 4-n-ω-alkenyloxybenzyl alcohole, 1.24 g (6 mmol) N,N'-dicyclohexylcarbodiimide (DCC) and catalytic amounts of 4-N,N-dimethylaminopyridine (DMAP) in 100 ml dry methylene chloride is stirred for 48 hours, after that processed as described for 2a and recrystallized from ethanol. Yields: 35-47%

5$_3$: ^{1}H-NMR (200 MHz, $CDCl_3$): δ = 0,83-0,90 (t, 6H, 2x $C\underline{H}_3$), 1,17-1,43 (m, 20H, 2x $(CH_2)_5$), 1,69-1,86 (m, 4H, 2x CH_2-$C\underline{H}_2$-CH_2-O-), 3,96-4,04 (t, 4H, 2x O-$C\underline{H}_2$-CH_2-), 4,49-4,53 (d, 2H, O-$C\underline{H}_2$-CH=CH_2), 5,24 (s, 2H, COO-$C\underline{H}_2$-

Ar), 5,28-5,44 (m, 2H, C$\underline{H}_2$=CH-), 5,93-6,12 (m, 1H, CH_2=C$\underline{H}$-CH_2), 6,84-8,12 (m, 11H, Ar)

Hydrosilylation reaction to prepare P3 and P5

0,01 mol of the monomers 3 or 5 and 0.6 g (0,032 mmol) of polymethylhydrogensiloxan (MERCK) are solved in 5 ml dry toluene. 0,05 M solution of $H_2PtCl_6 \cdot 6H_2O$ in dry isopropanol (1 droplet) is given to this clear solution and the mixture is allowed to stand at 100 °C until no Si-H-signal (at 2140 cm^{-1}) can be detected by IR-spectroscopic investigations.

The polymer is precipitated into methanol and purification is effected by precipitation of the polymer from dichloromethane solution with methanol. This process is repeated until the alkene precursors can not be detected by tlc. The product is given over a short column of Al_2O_3, eluent is chloroform, to remove residue of the catalyst. The pure polymer is dried in vacuo in the isotropic state.

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