

## Copolymers

### Synthesis and Anionic Polymerization of 2-Isopropenylquinoline

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#### Summary

2-Isopropenylquinoline has been synthesized, and anionic homopolymerization has been performed with *n*-butyllithium and with dibutylmagnesium, yielding polymers with high glass transition temperatures, with  $M_n$  ranging from 3700 to 210300. Molecular heterogeneities have been determined by GPC.  $M_w$  has been measured by light scattering. The glass transition temperature for infinite molecular weight is 475 K. The ceiling temperature, 367 K, was calculated from  $^1\text{H-NMR}$  spectra recorded from living poly-(2-isopropenylquinoline) at different temperatures. Two- and threeblock-copolymers have been obtained by initiating 2-isopropenylquinoline with living polybutadiene.

#### Introduction

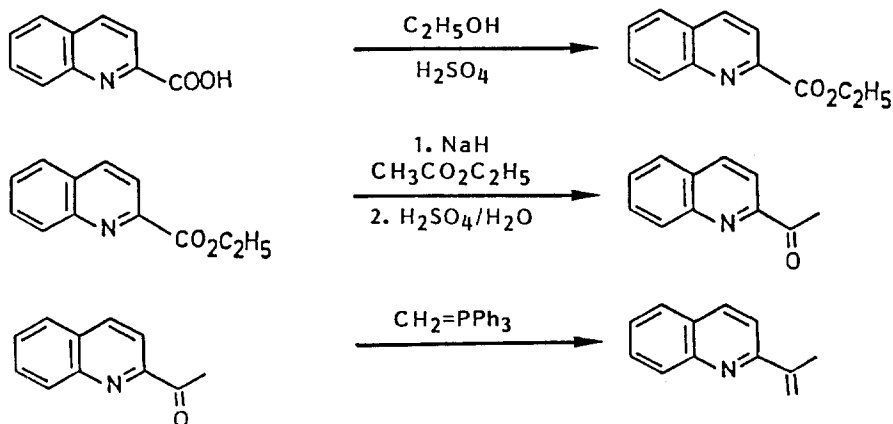
2-Isopropenylquinoline (2-IPCh) disappeared into oblivion after failing to homopolymerize or to copolymerize this monomer in 1948 <sup>1) 2)</sup>. Basing on recent knowledge it has been supposed that 2-IPCh may be accessible to anionic polymerization, analogous to other isopropenyl substituted aromates.

In order to ensure the purity required for anionic polymerization, a new synthesis for 2-IPCh had to be developed.

#### Experimental

##### Monomer Synthesis

##### Synthesis Route



Quinoline-2-carbonic acid ethylester

100 ml (0.58 mol) quinoline-2-carbonic acid is heated under reflux for 5 hrs with 250 ml absolute ethanol and 22 ml (0.41 mol) conc.  $\text{H}_2\text{SO}_4$ , under moisture exclusion. 20 g molecular sieve, 3 A, is added to the homogenous solution after 2.5 hrs. The alcohol is removed essentially by distillation, and the residual is poured into ice water, neutralized with  $\text{Na}_2\text{CO}_3$  and extracted with  $\text{CH}_2\text{Cl}_2$ . After drying over  $\text{MgSO}_4$  and removal of solvent by distillation the product is distilled under oil pump vacuum.

Conversion 77.3 g = 70.5%,  $K_p3 = 132^\circ\text{C}$

2-Acetylquinoline

10.8 g (0.45 mol) NaH is weighted as 55% wax dispersion. The wax is removed by decanting with n-pentane. Under  $\text{N}_2$  as protection gas a mixture of 77.3 g (0.41 mol) quinoline-2-carbonic acid ethylester and 39.8 g (0.45 mol) acetic ester is poured quickly into a suspension of the NaH in about 100 ml hexane. The reaction is started by careful heating under stirring, with subsequent cooling with methanol / dry ice. The yellow die formed under vigorous foaming is dissolved in 25%  $\text{H}_2\text{SO}_4$  (3 mol per mol ester), washed in hexane twice and heated directly for 1 hr to  $100^\circ\text{C}$  for decarboxilation. After neutralization with  $\text{Na}_2\text{CO}_3$  extraction is performed with  $\text{CH}_2\text{Cl}_2$ , with subsequent drying over  $\text{MgSO}_4$  and removal of the solvent by distillation. From the residual red solid the product is received by sublimation in the form of white crystals.

Conversion 38.5 g = 56% ,  $F_p = 52^\circ\text{C}$

$^1\text{H-NMR}$ :  $\delta = 7.5 - 8.5$  ppm (aryl),  $\delta = 2.95$  ppm (methyl). FTIR:  $1688\text{ cm}^{-1}$  (C=O)

2-Isopropenylquinoline

Three sets of experiments have been examined. The optimal conditions are described:

1.54 g NaH (0.064 mol) are applied as a 55% waxy dispersion, the wax being removed as described before. 30 ml dry DMSO are added dropwise under a nitrogen atmosphere. After stirring for 1 hr at  $80^\circ\text{C}$  and ending of  $\text{H}_2$ -development 24.3 g (0.068 mol) methyl triphenyl phosphonium bromide in 50 ml DMSO is added at room temperature. 10.8 g (0.068 mol) 2-acetylquinoline in concentrated DMSO-solution is dropped than into the freshly prepared ylide solution at  $0^\circ\text{C}$ . After further stirring 2 hrs in the ice bath and for 12 hrs at  $65^\circ\text{C}$  the solution is poured into 75 ml water, and the product is extracted with pentane. After drying over  $\text{Na}_2\text{SO}_4$  and distilling the solvent a slightly yellow coloured oil is obtained, which contains about 5% 2-acetylquinoline besides the 2-isoprenylquinoline. For the removal of the remaining ketone the raw product is stirred for 24 hrs at room temperature in 40 ml methanol with 1.7 g (0.044 mol)  $\text{NaBH}_4$  and 0.17 g (0.003 mol)  $\text{NaOCH}_3$ . After largely removing the solvent by distillation the product is extracted with pentane after adding 50 ml water. After drying with  $\text{Na}_2\text{SO}_4$  and distilling of the solvent 7.3 g product remained. Very pure 2-IPCh is obtained by sublimation, in the form of nice colourless crystals.

Conversion 6 g = 56%,  $F_p = 33^\circ\text{C}$

$^1\text{H-NMR}$ :  $\delta = 7.2-8.2$  ppm (aryl),  $\delta = 5.45$  and  $5.9$  ppm (vinyl) and  $\delta = 2.4$  ppm (methyl)  
FTIR: no absorption at  $1688\text{ cm}^{-1}$

Polymerization

About 10 ml degassed toluene, dried over styryl lithium, is condensed each time onto 0.5 g 2-IPCh in a high vacuum line. After degassing the solution twice n-butyllithium (1.6 ml solution in hexane, Merck Nr. 818874) is added by injection in  $\text{N}_2$  counter-current at room temperature. The fastly developed deep red-violet solution is polymerized at  $-78^\circ\text{C}$  for 1 hr. The living polymeric anions are terminated with few methanol, and the polymer is precipitated in methanol. Two samples have been polymerized with dibutylmagnesium (0.6 ml solution in heptane, Alfa Nr. 89746), following the procedure as described.

### NMR - Analysis for the Determination of the Ceiling - Temperature

In a vacuum line 4.7 ml perdeuterated toluene are dried with styryllithium and degassed and condensed subsequently onto 319 mg (1.9 mmol) repeatedly sublimated 2-IPCh, in a graduated ampoule with fused on NMR tube. The monomer solution is degassed twice again, and polymerization is initiated by injecting four drops of n-butyllithium solution (1.6 ml in hexane) in N<sub>2</sub> counter-current. The reaction ampoule containing the living polymer solution is melted off in vacuo. Part of the solution is poured into the NMR-tube, which is melted off also. Temperature variable <sup>1</sup>H-spectra are recorded and evaluated with this living polymer solution of known concentration.

## Results and Discussion

### Characterization of Polymers

Number average molecular weights have been determined by vapour pressure osmosis in CHCl<sub>3</sub>, besides the high molecular one. Molecular heterogeneities and weight average molecular weights have been analyzed by GPC, with calibration via polystyrene. For the high molecular weight sample M<sub>w</sub> has been determined by light scattering. The refractive index increment has been measured with a differential refractometer: 0.30 ml/g in THF at 436 nm at 25°C. For this high molecular weight sample, M<sub>w</sub> = 463000, M<sub>n</sub> = 210000, the second virial coefficient of osmotic pressure, A<sub>2</sub>, has been found 4.17·10<sup>-5</sup> ml/g<sup>-2</sup>, the quadratic radius of gyration <s<sup>2</sup>> = 2.53·10<sup>11</sup> cm<sup>2</sup>. Molecular weights and heterogeneities are presented in the table, besides tacticities and glass transition temperatures.

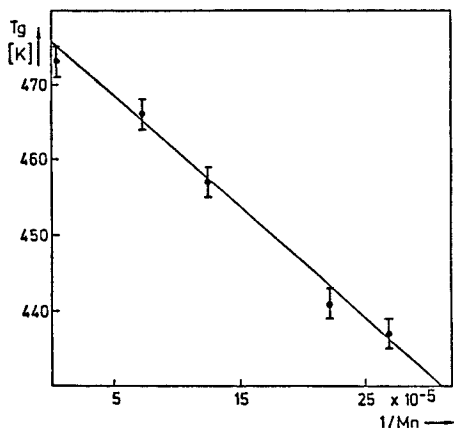
The polymers are colourless powders, which are soluble in benzene, toluene, CH<sub>2</sub>Cl<sub>2</sub>, CHCl<sub>3</sub> and THF, swell in ethylmethyl ketone, are not soluble in acetone, ethanol and aliphatic hydrocarbons. The molar extinction coefficient is ε = 2927 l/mol·cm in THF for λ = 319 nm.

**Table 1:** Molecular weights, tacticities and glass transition temperatures of the PIPCh's

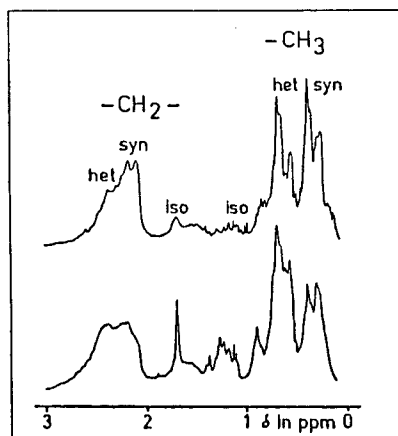
Initiator	M <sub>n</sub>	M <sub>w</sub>	U	Triads/%			T <sub>g</sub> /K
				iso	hetero	syndio	
n-Buli	3700	4500	0.22	15	55	30	437
n-Buli	4500	5400	0.20				
n-Buli	13900	17500	0.26				466
n-Buli	15100	18700	0.24				
n-Buli	210000	463000	1.20	20	45	35	473
Bu <sub>2</sub> Mg	4500	4900	0.08	4	48	48	441
Bu <sub>2</sub> Mg	8000	8800	0.10	9	48	43	457

Glass transition temperatures, T<sub>g</sub>, have been determined via DSC. Values between 437 and 473 K have been extrapolated for zero heating rate. The plot T<sub>g</sub> versus 1/M<sub>n</sub> is linear within experimental error (Figure 1), corresponding to the data for poly-(2-isopropenylnaphthalene) (494 K<sup>3</sup>). Extrapolation to infinite molecular weight yields T<sub>g∞</sub> = 475 K, this value being situated between those for α-methylstyrene (458 K<sup>4</sup> 5) and poly-(2-isopropenylnaphthalene) (494 K<sup>3</sup>).

The evaluation of the proton resonances of the α-methyl group turned out to be favourable for evaluation of tacticity<sup>6)-10</sup>. Consequently, we tried to evaluate the tacticity of poly-(2-isopropenylquinoline) by <sup>1</sup>H-NMR spectroscopy, in dependence on molecular weight and gegenion, during anionic polymerization. Spectra were recorded in perdeuterated nitrobenzene at 400 K (Figure 2). Assignment of triad signals of the α-methyl group has been performed in an analogous way to poly-(α-methylstyrene)<sup>6) 9) 10</sup> and poly-(2-isopropenylnaphthalene)<sup>3</sup>: Isotactic triads are absorbing at 1.2 ppm, heterotactic ones at 0.8 and syndiotactic ones at 0.4 ppm.



**Figure 1:** Glass transition temperature versus reciprocal  $M_n$  for poly-(2-isopropenylquinoline)s



**Figure 2:** 300 MHz  $^1\text{H-NMR}$  spectra of poly-(2-isopropenylquinoline)s. Upper trace:  $M_n = 4500$  ( $\text{Bu}_2\text{Mg}$ ), lower trace:  $M_n = 3700$  ( $\text{Buli}$ )

Additionally it has been also tried to assign the methylene signals between 1.5 and 2.5 ppm to the respective triads by comparison with the spectra as interpreted via methyl group resonances: Thus, syndiotactic triads are absorbing at 2.4, heterotactic ones at 2.2 and isotactic ones at 1.6 ppm. The triad concentrations as derived by integration of the methyl signals are given in the table for four of the polymers.

All PIPCh samples are essentially atactic. Mg as gegenion favours syndiotactic triads, whereas Li favours isotactic ones. Atactic triads are ranging around 50% in all cases. Isotactic triads are favoured with increasing molecular weight, in a similar way as for poly-( $\alpha$ -methylstyrene)<sup>6)</sup> and for poly-(2-isopropenyl-naphthalene)<sup>3)</sup>.

### Ceiling Temperature

The equilibrium concentration of monomer,  $[M]$ , is connected with the enthalpy of polymerization,  $\Delta H_{SS}$ , and the entropy of polymerization,  $\Delta S_{SS}$ , by

$$\Delta G_{SS} = RT \ln [M] = \Delta H_{SS} - T\Delta S_{SS} \quad (1)$$

$\Delta G_{SS}$  is the free enthalpy of polymerization and  $R$  the gas constant. The index *ss* denominates a 1 m monomer solution and dissolved polymer as the reference state. At the ceiling temperature  $T_C$   $\Delta G_{SS} = 0$  or  $[M] = 1 \text{ mol/l}$  must be valid per definition. The equilibrium concentration of monomer is determined at different temperatures. From the plot  $\ln [M]$  versus  $1/T$   $\Delta H_{SS}$ ,  $\Delta S_{SS}$  and  $T_C$  can be determined graphically from intercept, slope and extrapolation of the abscissa towards  $\ln [M] = 0$ .

From the living PIPCh solutions prepared as described ( $c = 0.402 \text{ mol/l}$ ) 90 MHz  $^1\text{H-NMR}$  spectra are recorded at different temperatures. The monomer content is calculated from the integrated olefinic doublet at 5.7 ppm. The results are given in table 2.

The plot  $\ln [M]$  versus  $1/T$  (Figure 3) shows the expected linearity at the lower temperatures, before the data bend downwards shortly before reaching the concentration applied. The ceiling temperature is determined as  $T_C = 367 \text{ K}$  by extrapolation towards  $\ln [M] = 0$ . The enthalpy of polymerization is  $\Delta H_{SS} = -22.5 \text{ J/mol}$ , the entropy  $\Delta S_{SS} = -61.4 \text{ J/mol}\cdot\text{K}$ . In table 3 these values are compared with the data of the known homologous monomers<sup>11)</sup>.

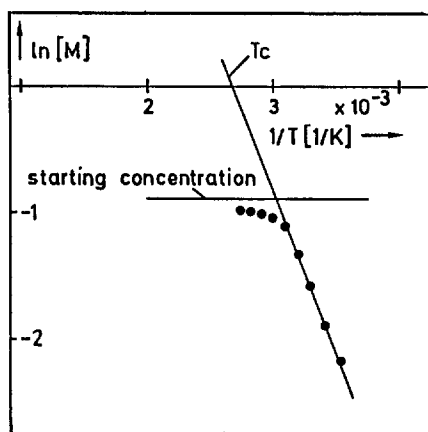


Figure 3: Graphic of polymerization equilibrium of 2-isopropenylquinoline

Table 2: Data for the determination of the polymerization equilibrium of 2-isopropenylquinoline

T / K	M / %	[M] / mol/l	ln [M]
283	28	0.112	- 2.19
293	36	0.147	- 1.92
303	50	0.202	- 1.60
313	65	0.263	- 1.34
323	81	0.327	- 1.12
333	85	0.343	- 1.07
343	88	0.357	- 1.03
353	90	0.364	- 1.01
363	90	0.364	- 1.01

Table 3: Polymerization equilibrium data

Monomer	$\Delta H_{SS}$ / kJ/mol	$\Delta S_{SS}$ / J/mol·K	$T_C$ / K	$T_C$ / °C
$\alpha$ -Methylstyrene	- 35,6	- 128.1	277.4	+ 4.2
2-Isopropenyl-naphthalene	- 36.2	- 121.8	297.1	+ 23.9
2-Isopropenylquinoline	- 22.5	- 61.4	367	+ 94

### Blockcopolymers with Butadiene

By initiating 2-IPCh with living polybutadienyl anions in toluene diblock copolymers are obtained. Because, vice versa, living poly-(2-IPCh) does not initiate butadiene in toluene, different triblock copolymers have been obtained by coupling 2-IPCh with living polybutadiene, which has been started bifunctionally in THF. Details of the synthesis and of the properties of those interesting thermoreversible elastomers will be reported in a following paper.

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