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4-Vinylphthalic anhydride

A new monomer for reactive homo- and copolymers*

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Summary

4-Vinylphthalic anhydride can be prepared from phthalic acid via bromination and subsequent olefination (Heck-reaction). Homo- and copolymerization with styrene was accomplished using AIBN as initiator. The copolymer compositions were determined by infrared-spectroscopy. The copolymerization parameters are r_S = 0,15 and r_{VPA} = 3,09, the corresponding Q, e values of 4-vinylphthalic anhydride are estimated as Q = 3,34 and e = 0,09.

Despite the fact that the molecular weights were rather low as a consequence of the reaction contions, the glass transition temperatures rise with increasing VPA content. The homopolymer has a glass transition temperature in the order of 226°C.

Introduction

Polymers containing reactive functional units are of considerable importance for the development of new functional and structural materials. Especially for the design of polymer blends the performance of the final material can be greatly enhanced by the ´in situ´ formation of block- and graft copolymers as compatibilizing agents during the melt blending process.

Such reactive functional units can be incorporated either by copolymerization of a corresponding monomer unit or by grafting onto a preformed polymer backbone. A typical example for a reactive functionality are acid anhydride units which can be incorporated by copolymerization or grafting of maleic anhydride.

During our studies on reactive polymers we have been searching for alternative moieties allowing the incorparation of anhydride units into a polymer backbone, without having the restrictions of the limited copolymerizability of maleic anhydride.

In the present and forthcoming papers of this series we will report on the homo- and copolymerization behaviour of 4-vinylphthalic anhydride with other vinyl monomers.

4-Vinylphthalic anhydride 1 is a monomer which can be regarded as the aryl-homologue of maleic anhydride. As an α-olefin it´s copolymerization behaviour should offer a much broader scope than maleic anhydride. However, 4-vinylphthalic anhydride can be considered as a ´forgotten´ monomer. In early work, Winslow followed an eight-step synthesis of the monomer [1,2]. He reported the synthesis of the

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*The polymerization behaviour of 4-vinylphthalic anhydride, part 1

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homopolymer without giving any characterization [3]. An alternative low yield multistep synthesis of 4-vinylphthalic anhydride was reported by Tahan [4].

A detailed study of the homo- and copolymerization behaviour of 4-vinylphthalic anhydride requires an efficient monomer synthesis. In the present paper we report the synthesis of the monomer and it´s homo- and copolymerization using styrene as the comonomer.

Experimental

Materials:

Laboratory grade reagents, solvents and palladium acetate were used as supplied, if not stated otherwise. N,N-dimethylformamide (DMF) was purified by destillation over diisocyanate (MDI). Styrene was predried with CaH_2 and destilled two times under reduced pressure and degased under vacuum three times, prior to the use in the copolymerization studies.

Synthesis of 4-vinylphthalic anhydride:

0,02 mol 4-bromophthalic acid [5], 0,17 mol triethylamine, $0{,}22 * 10^{-3}$ mol palladium acetate, $0{,}40 * 10^{-3}$ mol tri-o-tolylphosphine [6] and 70 ml N,N-dimethylformamide (DMF) were filled under argon-atmosphere into a 300 ml laboratory autoclave with magnetic stirring device. The Heck-reaction was performed at 40 bar ethylene-pressure at 100°C for at least 16 h [7,8]. The resulting suspension was filtered, cooled to -20°C and filtered once more after 12h to remove the $HN^+(C_2H_5)_3Br^-$. The surplus triethylamine was removed under vacuum. A calcium chloride solution was added dropwise causing the precipitation of the calcium-vinylphthalate, which was isolated by filtration.

The calcium-salt was dissolved in hot water and the pH was adjusted to about pH = 1,5 by addition of dilute hydrochloric acid. The solution is filtered and concentrated in a rotary evaporator. The product crystallizes from the solution at 4°C (refrigerator). The solid was recrystallized from water with a trace of hydrochinone. The yield of the pure acid is about 30%.

4-vinylphthalic anhydride was obtained by sublimation of 4-vinylphthalic acid according to Winslow [2,3].

Poly(4-vinylphthalic anhydride):

The radical homopolymerization of 4-vinylphthalic anhydride was carried out in acetonitrile at 90°C under N_2-atmosphere. The reaction time was 24 hours. During this period the polymer precipitated from the reaction mixture. The monomer concentration was about 0,25 mol/l and the molar ratio of monomer to AIBN was 30/1. The solid polymeric product was recovered by filtration, and purified by heating the solid in acetonitrile, in which the monomer is soluble but not the polymer. Poly-4-vinylphthalic anhydride was dried in vacuum at 60°C for three days.

P(S-co-4-VPA) copolymers:

The reaction (90°, acetonitrile, AIBN, [VPA + S] ≈ 0,25 mol/l; $\frac{[M]}{[AIBN]} \approx 30$)conditions were the same as in the case of homo-4-vinylphthalic anhydride. Six different compositions of styrene and 4-vinylphthalic anhydride were used (see Table 1). The mixtures were degased twice and heated to reflux for 3h. The copolymers were isolated by precipitation into methanol and dried under vacuum at 60°C for at least three days. The conversion was in the range of 25 % in all experiments.

Analysis:

IR-spectra were taken as KBr pellets (~1,6 mg/135 mg KBr) using a Bruker IFS 48 FT-IR-spectrometer at a resolution of 2 cm^{-1}. 32 scans were accumulated. For the analysis of the copolymer composition the spectra were normalized with respect to the total intensity of the aliphatic stretching vibration (spectral range from 2980 to 2810 cm^{-1}). This procedure was checked by analyzing a series of mixtures of poly-4-VPA and PS of known composition. The reference experiments showed that the molar absorbance of the aliphatic CH-stretching vibrations of PS and P(4-VPA) are the same within experimental error.

1H-NMR-spectra were recorded using a Bruker AC 200 NMR spectrometer (200 MHz; d_7-DMF, d_3-acetonitrile). Gel permeation chromatography (GPC) was performed in tetrahydrofurane with a set of 10 µm PL-Gel-columns (10^5, 10^4, 10^3 and 10^2 A with refractive index and UV detection at 254 nm, calibrator with PS standards. Measurements of differential scanning calorimetry were recorded with a Perkin Elmer DSC-7 (heating rate 20K/min.).

Results and discussion

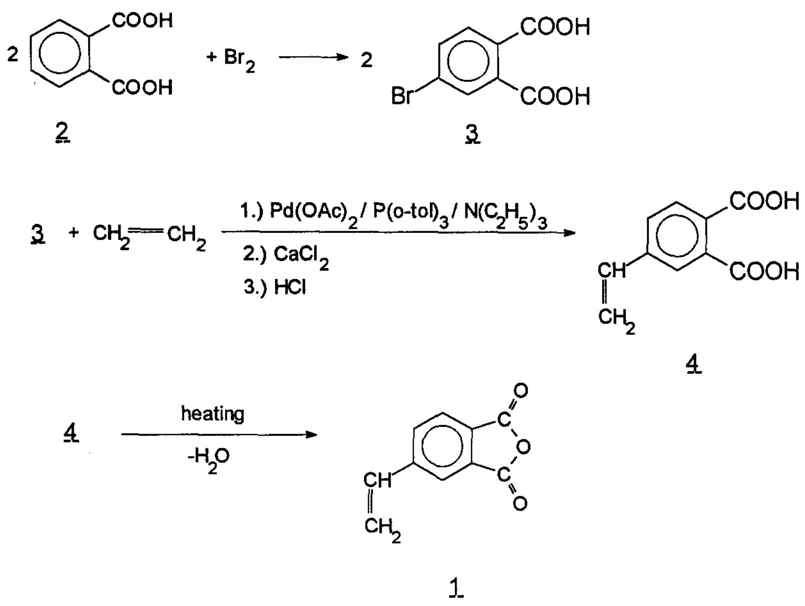
Monomer synthesis and characterization:

The synthesis of 4-vinylphthalic anhydride was accomplished via bromination of phthalic acid [5] followed by olefination with ethylene and final sublimation of 4-vinylphthalic acid as shown in reaction scheme 1. The olefination of 4-bromophthalic acid by the Heck-reaction was performed analogous to the synthesis of 4-vinylbenzoic acid [7,8], however isolation of the product became rather difficult. While the isolation of 4-vinylbenzoic acid is very simple - the reaction mixture can be diluted with water and 4-vinylbenzoic acid precipitates in diluted hydrochloric acid (pH=1,5), this procedure is not successful in the case of 4-vinylphthalic acid. First the calcium-salt had to be precipitated. The calcium-4-vinylphthalate was transfered into the corresponding acid. The 4-vinylphthalic acid was placed in a sublimation apparatus. At a vacuum of approximately $1 * 10^{-3}$ bar the sublimation tube was heated to 90°C in an oil bath. After several days light yellow crystals were scraped off the cold finger of the sublimation apparatus in a yield of about 60%. The product was stored over P_2O_5.

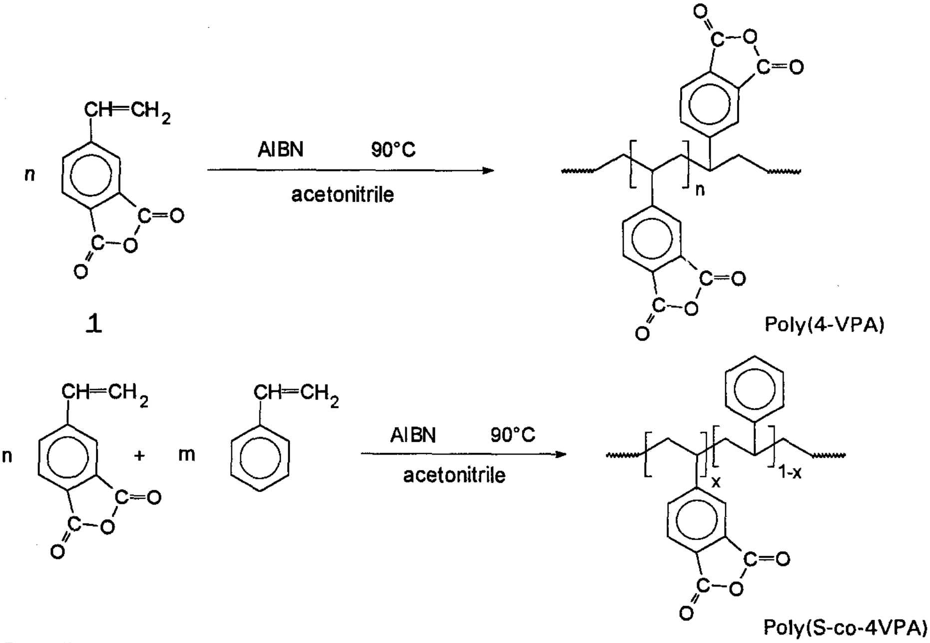
The monomer and the intermediate reaction products were characterized by ^{1}H-NMR-spectroscopy as well as by infrared-spectroscopy and elemental analysis. Figure 1a shows the ^{1}H-NMR-spectrum of 4-vinylphthalic anhydride. The signals of the three vinylic protons are at 5,60 ppm (d), 6,13 ppm (d) and 6,94 ppm (dd) and the aromatic protons are at 7,93 ppm (s) and 8,05 ppm (s). The light yellow crystals of 4-VPA melt at 86°C. Calc. for $C_{10}H_6O_3$: C, 68.9%; H, 3.45%. Found: C, 65.63%; H, 3.38%. 4-vinylphthalic anhydride was found to be soluble in N,N-dimethylformamide, N,N-dimethylacetamide and acetonitrile.

Synthesis of homo-and copolymers with styrene and their characterization:

The first homopolymerizations of 4-vinylphthalic anhydride (1) were carried out according to the prescription given by Winslow [2]. The radical polymerization was carried through at 90°C in acetonitrile under N_2 atmosphere using AIBN as initiator.



Reaction scheme 1



Reaction scheme 2

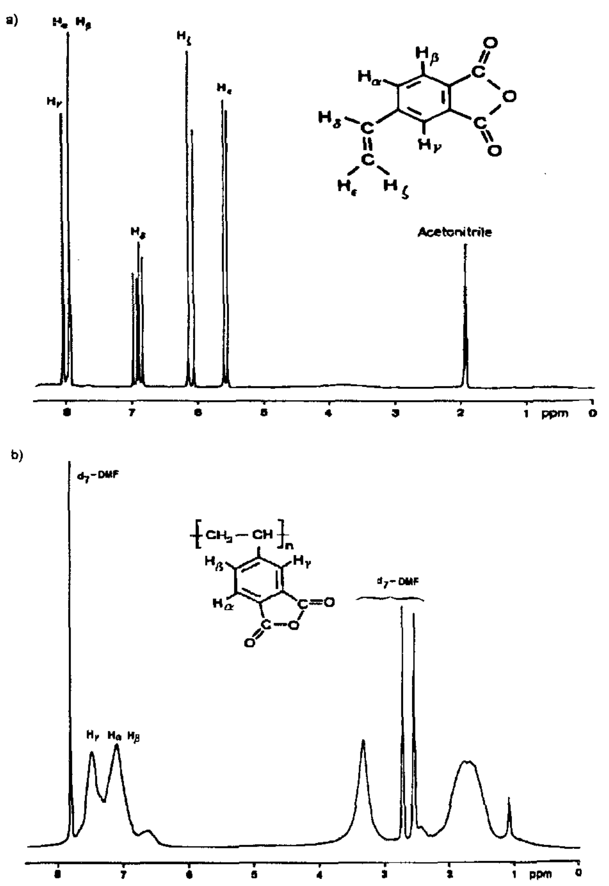


Figure 1: *200 MHz-^{1}H-NMR-spectrum of 4-vinylphthalic anhydride (a) in d_3- acetonitrile and the homopolymer (b) in d_7-N,N-dimethylformamide*

The NMR-spectrum of the raw product poly-(4-VPA) as it precipitated from the polymerizing solution showed a residue of monomer. Therefore the solid polymeric product was purified by heating the solid in acetonitrile, in which the monomer was soluble but not the polymer. Figure 1b shows the ^{1}H-NMR-spectrum of the purified poly-4-VPA - after complete removal of the monomer. Besides the DMF-solvent peaks at 2,55 ppm, 2,75 ppm, 3,35 ppm (H_2O in DMF) and 7,8 ppm only the broad signals of the polymer at 1,75 ppm (aliphatic protons) and at 7,1 ppm and 7,45 ppm (aromatic protons) are observed. Poly-(4-VPA) is soluble in N,N-dimethylformamide and N,N-dimethylacetamide and unsoluble in chloroform and tetrahydrofurane. Therefore the molecular weight could not be determined by GPC.

The glass transition temperature is 226°C (DSC, extrapolated to heating rate zero).

Copolymerizations of styrene and 4-vinylphthalic anhydride (1) were performed under the same conditions as the homopolymerization: acetonitrile, AIBN, 90°C. The yields of the polymerizations were kept around 27%. Thus the copolymerization parameters could only be determined after correcting for high yields.

One of the basic questions is, whether 4-VPA also shows a tendency towards alternation in copolymerizations as is known for maleic anhydride. In addition our main interest is in copolymers containing only small amounts of 4-VPA. NMR spectroscopy is not sensitive enough to determine the copolymer composition with sufficiently high accuracy. The method of choice is IR-spectroscopy.

After normalization to constant molar concentrations (see Experimental part), the spectra can be analyzed quantitatively. Figure 2 shows the IR-spectra of the different copolymers and poly(4-VPA) in the carbonyl stretching region. The infrared spectra show a continuous rise of the intensity of the carbonyl absorption with increasing 4-VPA content in the monomer mixture. This already indicates that 4-VPA has no tendency towards alternation in the copolymerization with styrene. In addition the copolymer always contains more 4-VPA than the copolymerization feed.

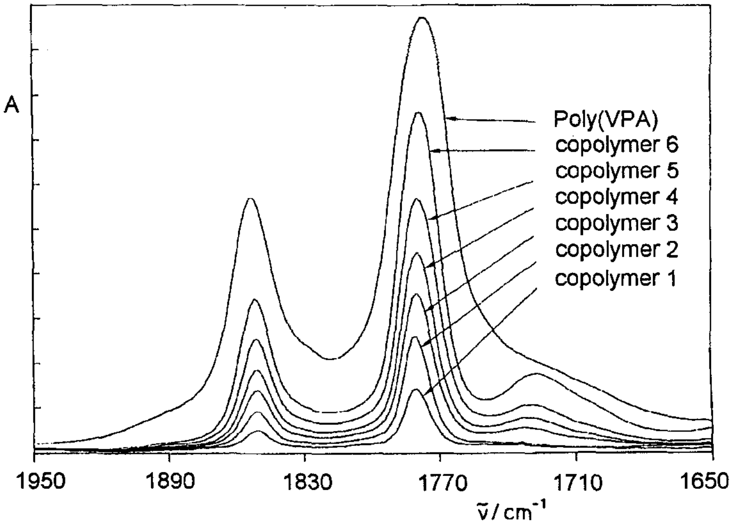


Figure 2: *Infrared-spectra of homo-and copolymers in the range from 1950-1650 cm^{-1}, normalized to equal molar concentrations of the repeating units.*

From integration of the carbonyl absorption from 1910 to 1820 cm-1 the molar ratio of 4-VPA in the copolymers (Table 1).is obtained. The copolymerization parameters were determined according to the method of Kelen and Tüdös [9,10]. Figure 3 shows the 'Kelen-Tüdös-plot' with α = 50,25. From the linear behaviour we first can conclude that the copolymerization is described adequately by the simple binary copolymerization modul. The copolymerization parameters are r_S = 0,15 and r_{VPA} = 3,09 and $r_S * r_{VPA}$ = 0,45.These values are typical of nonideal nonazeotrope copolymerizations. Fig.4 shows the copolymerization diagram which has a strong convex curvature. Obviously 4-VPA is more reactive in radical polymerizations than styrene. As a consequence a chemically heterogeneous polymer will be formed in batch polymerizations conducted to high yields. From r_{VPA} and r_S the Q, e parameters according to the Alfrey-Price scheme can be evaluated (Q = 3,34; e = 0,09). These data indicate that 4-VPA is more resonance stabilized than styrene (Q_S= 1.0) and that the electron withdrawing character of the anhydride moiety is balanced by the electron donating phenyl ring.

Table 1: *Copolymerizations of 4-VPA and styrene (acetonitrile, AIBN, 90°)*

Exp	polymer	mol% 4-VPA in monomer mixture	mol% 4-VPA in copolymer	weight% 4-VPA in copolymer
1	P(S-co-4-VPA- 10)	1,47	6,6	10,5
2	P(S-co-4-VPA- 18)	3,08	11,6	18,0
3	P(S-co-4-VPA- 27)	6,26	18,1	27,0
4	P(S-co-4-VPA- 36)	9,26	25,6	36,5
5	P(S-co-4-VPA- 47)	13,09	35,1	47,5
6	P(S-co-4-VPA- 67)	28,16	55,3	67,4
7	Poly-4-VPA	100	100	100

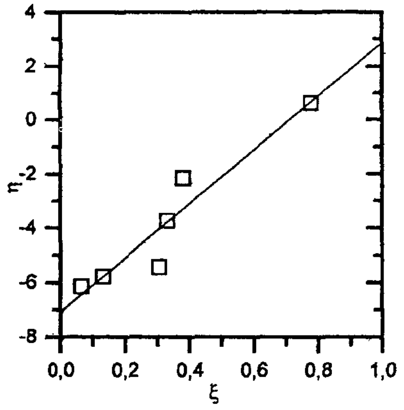


Figure 3: *'Kelen-Tüdös-plot'. Extrapolation to ξ=0 and ξ=1 gives -r_2/α and r_1*

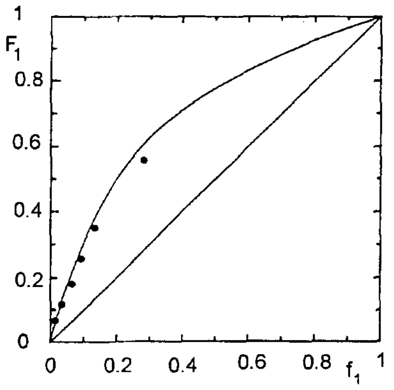


Figure 4: *Copolymerization diagramm: Mole fraction of 4-VPA in copolymers(F_1) and feed stock (f_1)*

Owing to the high reaction temperature used in our polymerization according to [1-3] only low molar mass material was formed. Molecular weights of the polymers as determined by gel permeation chromatography are summarized in Table 2. The apparent decrease of the molecular weight with increasing 4-VPA content may result from a change in the hydrodynamic behaviour in comparison to PS (GPC-standard).

From differential scanning calorimetry first results concerning the bulk properties were obtained. With increasing 4-VPA content the glass transition temperatures of the copolymers increases considerably; despite the low molecular weights. The glass temperatures as obtained after extrapolation to heating rate zero are summarized in Table 2.

Table 2: *Molecular weights and glass temperatures of the homo-and copolymers as determined by GPC (THF) using polystyrene calibration and by DSC at a heating rate of 20K/min*

polymer	T_g [°C]	M_n2)
P(S-co-4-VPA- 10)	91	5700
P(S-co-4-VPA- 18)	107	6100
P(S-co-4-VPA- 27)	116	4300
P(S-co-4-VPA- 36)	128	3500
P(S-co-4-VPA- 47)	137	2900
P(S-co-4-VPA- 67)	160	2200
Poly-4-VPA1)	226	-

1) Poly-4-VPA is not soluble in THF and $CHCl_3$, ;2) determined by GPC with respect to PS-calibration;

Conclusions

The work presented in the present paper shows that vinyl phathlic anhydride is readily available following a new synthetic route. The copolymerization experiments indicate that the different reactivity of 4-VPA in comparison to maleic anhydride may make this monomer useful in a variety of copolymers either to increase the glass transition temperature or to take advantage of the acid anhydride functionality.

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