# Free radical copolymerization of 1-vinyl naphthalene with styrene, methyl methacrylate, and acrylonitrile

D. Braun[1]), A. Essmail Pour, and W. K. Czerwinski

[1]) Deutsches Kunststoff-Institut, Darmstadt, FRG

*Abstract:* Investigations on free radical copolymerization of 1-vinyl naphthalene (1-VNph, monomer $M_2$) with styrene (St), methyl methacrylate (MMA) and acrylonitrile (AN) (monomers $M_1$) in bulk at 60 °C with AIBN as initiator are presented. Relative reactivity ratios were calculated by the Kelen-Tüdös method yielding: $r_{St} = 0.70 \pm 0.23$ and $r_{1-VNph} = 2.02 \pm 0.40$ for system St/1-VNph; $r_{MMA} = 0.32 \pm 0.10$ and $r_{1-VNph} = 0.57 \pm 0.07$ for system MMA/1-VNph and $r_{AN} = 0.11 \pm 0.03$ and $r_{1-VNph} = 0.45 \pm 0.09$ for system AN/1-VNph. $Q, e$ values for 1-VNph according to Alfrey, Price scheme were calculated to $Q_{1-VNph} = 1.02$, $e_{1-VNph} = -0.62$.

*Key words:* Free radical copolymerization; 1-vinyl-naphtalene; styrene; methylmethacrylate; acrylonitril; relative reactivity ratios; Q- and e-values.

## Introduction

One of the most interesting aromatic homologue of styrene is vinyl naphthalene with vinyl groups at the positions 1 or 2, respectively. The kinetics of the free radical homopolymerization of 1-vinyl naphthalene (1-VNph) [1] and its binary copolymerization with styrene (St) [2] has been published. The reactivity of 2-vinyl naphthalene (2-VNph) was investigated in its copolymerization with styrene and methyl methacrylate (MMA) [3]. Both isomers show a very similar reactivity which is higher against the styryl or its own radical attack than the reactivity of styrene. This finding was confirmed recently by Bevington et al. [4,5] using azoisobutyronitrile (AIBN) ^{13}C-enriched in its methyl groups or benzoylperoxide (BPO) labelled with ^{14}C and tritium as initiators. Reactivity of 2-VNph was compared to the reactivities of MMA and 2-i-propenyl naphthalene [4] or to styrene [5]. The monomers containing the naphthyl group were found appreciably more reactive against primary initiator radicals than styrene.

In the present paper copolymerization experiments of 1-VNph ($M_2$) with St, MMA and acrylonitrile (AN) (as monomers $M_1$) are presented with the aim to obtain information about the reactivity of 1-VNph.

For this purpose relative reactivity ratios $r_i$ for the classical copolymerization model [6,7] were determined using the linearization method of Kelen and Tüdös (KT method) [8–11]. On the basis of these data, reactivity increments $Q$ and $e$ according to Alfrey and Price [12] were calculated.

## Experimental part

1-VNph was prepared by a procedure described in [1] from commercial 1-bromo naphthalene via Grignard reagent and addition of acetaldehyde and hydrolysis via 1-(1-naphthyl) ethan-1-ol (carbinol). The carbinol was kept in darkness because of its photodestruction leading from a white solid carbinol (m.p. 62–63 °C) to a dark colored compound. The carbinol was dehydrated as described in [2] by passing its vapors through a 30 cm $Al_2O_3$ column at 350 °C under vacuum. Commercial $Al_2O_3$ for chromatography neutral and acid, mixed 1:1, was used. It was immobilized in the column by means of glass wool and glass rings. The product was dried over $CaCl_2$, $CaH_2$ and redistilled after addition of a portionn of triphenylverdazyle [13,14] as inhibitor to prevent thermal polymerization.

1-VNph distilled at 85–92 °C (2.5–3 torr). The global yield of the synthesis was about 57%.

The pure 1-VNph showed the following ^{1}H-NMR signals:
7 aromatic protons: 7–8 ppm;
$\alpha$-proton quadruplet: 7–8 ppm (not visible);
trans-$\beta$-proton (quadruplet): 5,20; 5,24; 5,44; 5,48 ppm and

Table 1. Copolymerization of the system styrene $(M_1)$/1-vinyl naphthalene $(M_2)$ in bulk at 60 °C with AIBN as initiator ([AIBN] = 3.8 · $10^{-2}$ mol · $l^{-1}$, reaction volume 10 ml)

| Nr. | Monomer mol fraction 1-VNph $(M_2)$ | Polymer mol fraction 1-VNph $(m_2)$ | | AIBN g | $tp^{c)}$ min | Conversion wt.-% | $Rp \cdot 10^{4\,d)}$ mol · $l^{-1}$ · $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | elem.anal.[a] | IR analysis[b] | | | | |
| St/1-VNph/1 | 0.1423 | 0.1776 | 0.2198 | 0.0505 | 30 | 9.37 | 3.22 |
| St/1-VNph/2 | 0.2805 | 0.3789 | 0.3704 | 0.0505 | 60 | 8.41 | 1.60 |
| St/1-VNph/3 | 0.4107 | 0.5640 | 0.5587 | 0.0506 | 60 | 8.03 | 1.65 |
| St/1-VNph/4 | 0.5318 | 0.6772 | 0.6601 | 0.0508 | 60 | 8.27 | 1.82 |
| St/1-VNph/5 | 0.6452 | 0.7376 | 0.7168 | 0.0515 | 60 | 8.72 | 2.05 |
| St/1-VNph/6 | 0.7505 | 0.8553 | 0.8511 | 0.0509 | 60 | 8.70 | 2.15 |
| St/1-VNph/7 | 0.8441 | 0.9355 | 0.8970 | 0.0502 | 60 | 9.06 | 2.34 |
| St/1-VNph/8 | 0.9378 | 0.9832 | 0.9524 | 0.0504 | 120 | 9.14 | 1.22 |

[a] H analysis; [b] from aromatic absorption bands at 700 cm$^{-1}$ (styrene) and 780 cm$^{-1}$ (1-VNph); [c] polymerization time; [d] rate of polymerization

cis-$\beta$-proton (quadruplet): 5,37; 5,41; 5,75; 5,79 ppm.

Styrene, MMA, AN and solvents were purified by standard procedures.

AIBN was recrystallized from methanol and dried under vacuum.

Copolymerizations were carried out in glass ampoules under $N_2$ atmosphere in bulk with AIBN as initiator. The reacting components were degassed by threefold freeze-thawing cycles and then immersed in a water bath at 60 °C + 0.1 °C for a given reaction time.

The copolymers were separated by precipitation in methanol and reprecipitated from chloroform solution. Copolymer compositions were determined by elemental analysis. Additional IR spectral analysis was performed for the system St/1-VNph and MMA/1-VNph. The system AN/1-VNph was investigated by means of $^1$H-NMR spectroscopy. $^1$H-NMR spectra were obtained in CDCl$_3$ or $d_6$-DMSO (system AN/1-VNph) solutions or in a mixture of both solvents.

IR spectra were recorded with Perkin Elmer instrument type 457; $^1$H-NMR spectra were obtained by means of a Varian spectrometer EM 360, 60 MHz.

## Results and discussion

### Copolymer composition

1-VNph is well miscible with St, MMA, and AN and most copolymerizations proceeded in homogenous solution of the copolymer in monomer feed. Reaction conditions and copolymer compositions found from elemental and spectral analysis are presented in Tables 1 to 3 for systems St/1-VNph, MMA/1-VNph and AN/1-VNph, respectively. For runs with high AN content in system AN/1-VNph/1 and 2 polymer precipitation from the reaction mixture was observed. $^1$H-NMR spectra of this series were taken from $d_6$-DMSO solutions or its mixture with CDCl$_3$. The composition of the obtained copolymers is presented as a function of the monomer freed in Fig. 1.

Table 2. Copolymerization of the system methyl methacrylate $(M_1)$/1-vinyl naphthalene $(M_2)$ in bulk at 60 °C with AIBN as initiator (reaction volume 10 ml)[a]

| Nr. | Monomer mol fraction 1-VNph $(M_2)$ | Polymer mol fraction 1-VNph $(m_2)$ | | AIBN g | $tp$ min | Conversion wt.-% | $Rp \cdot 10^5$ mol · $l^{-1}$ · $s^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | elem.anal.[b] | IR analysis[c] | | | | |
| MMA/1-VNph/1 | 0.1388 | 0.2410 | 0.3389 | 0.0500 | 45 | 2.04 | 5.03 |
| MMA/1-VNph/2 | 0.2505 | 0.3571 | 0.3704 | 0.0501 | 90 | 2.70 | 3.54 |
| MMA/1-VNph/3 | 0.3966 | 0.4852 | 0.4406 | 0.0507 | 90 | 2.79 | 3.85 |
| MMA/1-VNph/4 | 0.5198 | 0.5638 | 0.5348 | 0.0507 | 90 | 2.53 | 3.67 |
| MMA/1-VNph/5 | 0.6618 | 0.6724 | 0.6579 | 0.0514 | 90 | 3.39 | 5.18 |
| MMA/1-VNph/6 | 0.7888 | 0.7694 | 0.7353 | 0.0513 | 90 | 3.99 | 6.53 |
| MMA/1-VNph/7 | 0.8538 | 0.8298 | 0.7693 | 0.0504 | 90 | 4.14 | 7.12 |
| MMA/1-VNph/8 | 0.9464 | 0.9107 | 0.9175 | 0.0508 | 90 | 4.77 | 8.59 |
| 1-VNph | 1.0000 | 1.0000 | — | 0.0507 | 90 | 8.81 | 10.90 |

[a] symbols s. Table 1; [b] C analysis; [c] from carbonyl absorption band at 1730 cm$^{-1}$ (MMA) and aromatic absorption bands at 780 cm$^{-1}$ (1-VNph)

Table 3. Copolymerization of the system acrylonitrile $(M_1)$/1-vinylnaphthalene $(M_2)$ in bulk at 60 °C with AIBN as initiator (reaction volume 10 ml)[a])

| Nr. | Monomer mol fraction 1-VNph $(M_2)$ | Polymer mol fraction 1-VNph $(m_2)$ elem.anal.[b]) | NMR analysis[c]) | AIBN g | tp min | Conversion wt.-% | $Rp \cdot 10^5$ mol · l$^{-1}$ · s$^{-1}$ |
|---|---|---|---|---|---|---|---|
| AN/1-VNph/1 | 0.0215 | 0.0929 | — | 0.0165 | 30 | 0.60 | 1.89 |
| AN/1-VNph/2 | 0.0355 | 0.2326 | 0.1971 | 0.0178 | 60 | 0.57 | 0.94 |
| AN/1-VNph/3 | 0.0698 | 0.3255 | 0.3429 | 0.0163 | 60 | 0.75 | 1.37 |
| AN/1-VNph/4 | 0.1601 | 0.4107 | 0.4041 | 0.0161 | 60 | 1.00 | 2.08 |
| AN/1-VNph/5 | 0.3679 | 0.6201 | 0.5102 | 0.0169 | 90 | 1.66 | 2.77 |
| AN/1-VNph/6 | 0.6206 | 0.6363 | 0.6201 | 0.0166 | 90 | 1.02 | 2.00 |
| AN/1-VNph/7 | 0.7961 | 0.7483 | 0.7500 | 0.0168 | 90 | 1.80 | 4.11 |
| AN/1-VNph/8 | 0.9313 | 0.8575 | 0.8571 | 0.0166 | 180 | 2.73 | 3.88 |

[a]) symbols s. Table 1; [b]) C analysis; [c]) from separation of aromatic proton signals (1-VNph) and aliphatic proton signals

In the system St/1-VNph the 1-VNph units dominate in the copolymer over the whole range of the monomer feed composition. Both other systems MMA/1-VNph and AN/1-VNph show azeotropic points in the region between 60 and 65 mol-% 1-VNph in the monomer feed tending very slighly to the alternation.

As the agreement between the elemental and spectral analysis for all three systems is satisfying, the results from both analytical methods were used together for calculations of relative reactivity ratios $r_1 = k_{P11}/k_{P12}$ and $r_2 = k_{P22}/k_{P21}$ according to the KT method [11] and yielded the following values for $r_1$ and $r_2$:

system St $(M_1)$/1-VNph $(M_2)$〉   $r_1 = 0.70 \pm 0.23$
$r_2 = 2.02 \pm 0.40$

MMA $(M_1)$/1-VNph $(M_2)$〉   $r_1 = 0.32 \pm 0.10$
$r_2 = 0.57 \pm 0.07$

AN $(M_1)$/1-VNph $(M_2)$〉   $r_1 = 0.11 \pm 0.03$
$r_2 = 0.45 \pm 0.09$

The reactivity ratios obtained here for St and 1-VNph are close to those reported [2] for the same monomer system $r_1 = 0.67$, $r_2 = 1.35$.

In Figs. 2–4 graphical KT transformations of the experimental data for each system are presented. Data for all monomer systems can be described by straight lines, which indicates that the two-parameter model may be applied for interpretation of the systems under consideration. The reactivity ratios resulting from the KT transformation were used for calculations of the copolymer composition as a function of the monomer

feed. From Fig. 1 generally a good agreement between the experiment and model can be observed.

By means of the measured relative reactivity ratios, $Q$- and $e$-increments for 1-VNph were calculated according to [12]. $Q$- and $e$-values for $M_1$ were taken from [15] as a basis. The calculated values for $Q$ and $e$ are as follows:
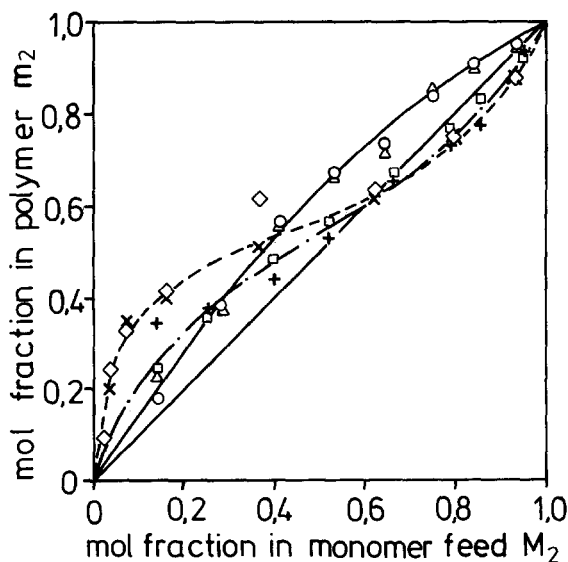


Fig. 1. Copolymerization diagram for the system: St $(M_1)$/1-VNph $(M_2)$ ○ elemental analysis, △ IR analysis, —— calculated with [9–12], $r_1 = 0.699$, $r_2 = 2.018$; MMA $(M_1)$/1-VNph $(M_2)$ □ elemental analysis, + IR analysis, — · — · — calculated with [9–12], $r_1 = 0.321$, $r_2 = 0.574$; AN $(M_1)$/1-VNph $(M_2)$ ◇ elemental analysis, × $^1$H-NMR analysis, - - - - calculated with $r_1 = 0.094$, $r_2 = 0.471$; (experimental conditions s. Tables 1–3, respectively)
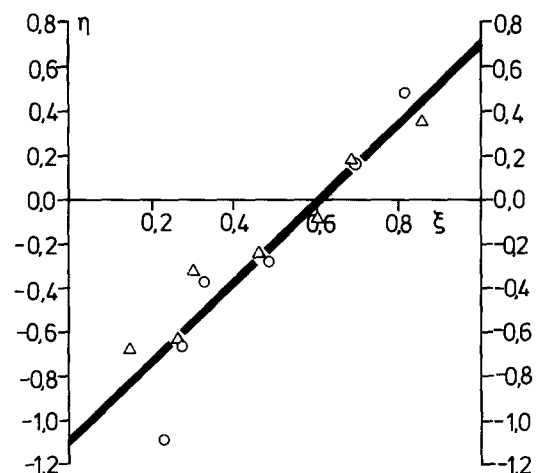
Fig. 2. KT-transformation of the data from Table 1 for the system styrene $(M_1)$/1-vinyl naphthalene $(M_2)$, $\delta^2 = 0.066$, $Q = 0.635$, $\alpha = 1.835$, $r_1 = 0.699 \pm 0.233$, $r_2 = 2.018 \pm 0.401$, $\bigcirc$ elemental analysis, $\triangle$ IR analysis
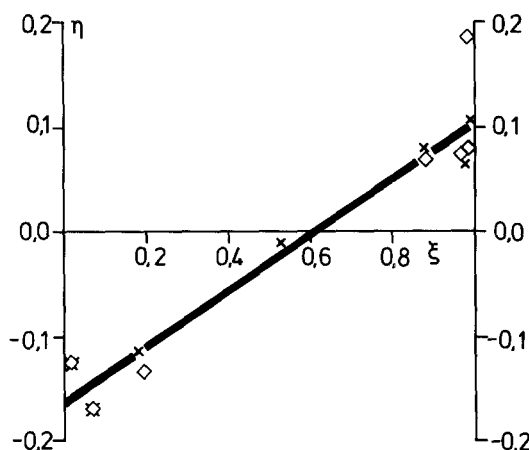


Fig. 4. KT-transformation of the data from Table 3 for the system acrylonitrile $(M_1)$/1-vinyl naphthalene $(M_2)$, $\delta^2 = 0.052$, $Q = 0.657$, $\alpha = 2.772$, $r_1 = 0.107 \pm 0.028$, $r_2 = 0.451 \pm 0.088$, $\diamond$ elemental analysis, $\times$ $^1$H-NMR analysis

system St/1-VNph:

$Q_{St} = 1.0$ [15, 18]    $Q_{1\text{-VNph}} = 1.09$
$e_{St} = -0.8$    $e_{1\text{-VNph}} = -0.46$

system MMA/1-VNph:

$Q_{MMA} = 0.78$ [15]    $Q_{1\text{-VNph}} = 1.44$
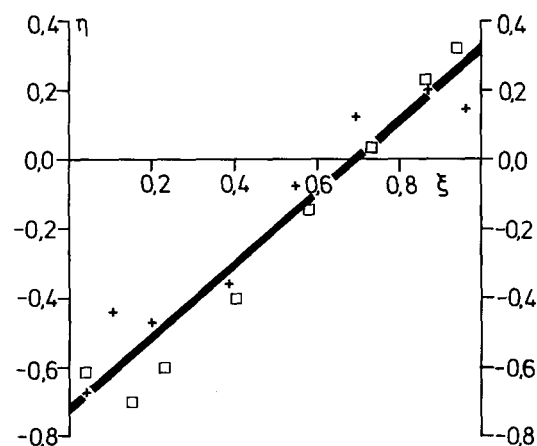$e_{MMA} = +0.40$    $e_{1\text{-VNph}} = -0.90$



Fig. 3. KT-transformation of the data from Table 2 for the system methyl methacrylate $(M_1)$/1-vinyl naphthalene $(M_2)$, $\delta^2 = 0.038$, $Q = 0.447$, $\alpha = 0.799$, $r_1 = 0.321 \pm 0.096$, $r_2 = 0.574 \pm 0.073$, $\bigcirc$ elemental analysis, $+$ IR analysis

system AN/1-VNph:

$Q_{AN} = 0.48$ [15]    $Q_{1\text{-VNph}} = 0.53$
$e_{AN} = +1.23$    $e_{1\text{-VNph}} = -0.51$

Average values for Q and e for 1-VNph are:

$Q_{1\text{-VNph}} = 1.02$
$e_{1\text{-VNph}} = -0.62$.

Comparing 1-VNph to St, it should be stated that both monomers show very similar copolymerization behavior. The reactivities of these monomers are close together, because the vinyl groups are directly attached to aryl groups. Owing to the presence of the aryl groups both monomers are highly susceptible to addition of radicals leading to relatively stabile adducts. 1-VNph is a little more reactive than St because of its higher resonance stabilization ($Q_{1\text{-VNph}} > Q_{St}$). 1-VNph radicals are, by the same reason, less reactive than St radicals. For the polymerization rate the reactivity of the growing radical is decisive. In agreement with [2], it was observed that the rate of 1-VNph homopolymerization is lower than the rate of St homopolymerization.

Similarly, the polarization factors e of both monomers are close. In analogy to the systems St/ MMA and St/AN both systems containing 1-VNph instead of St show a slight tendency to alternating

polymers and exhibit azeotropic points. This analogy to styrene was also observed on copolymerization of 2-VNph with other electron accepting monomers as N-methyl citraconimide [16] and methacrylic acid [17] to alternating copolymers.

It seems to be valid that the reactivity of 1-VNph is not mainly controlled by steric factors in comparison with styrene but by the electronic structure of this monomer. The last factor is dominated by the presence of the naphthyl group with its ability to high resonance stabilization.

### References

1. Loshaek S, Broderick E, Bernstein Ph (1959) J Polym Sci 39:223
2. Loshaek S, Broderick E (1959) J Polym Sci 39:241
3. Price CC, Halpern BD, Voong S-T (1953) J Polym Sci 11:575
4. Barson CA, Bevington JC, Breuer SW, Huckerby TN (1988) Polym Bull 20:31
5. Bevington JC, Ayrey G (1987) Eur Polym J 23:497
6. Alfrey T, Goldfinger G (1944) J Chem Phys 12:205
7. Mayo FR, Lewis FM (1944) J Am Chem Soc 66:1594
8. Kelen T, Tüdös F (1975) J Macromol Sci, Chem A9:1
9. Tüdös F, Kelen T, Földes-Berezsnich T, Turcsanyi B (1976) J Macromol Sci, Chem A10:1513
10. Tüdös F, Kelen T (1981) J Macromol Sci, Chem 16:1283
11. Kelen T, Tüdös F, Turcsanyi B (1980) Polym Bull 2:71
12. Alfrey T, Price C (1947) J Polym Sci 2:101
13. Kuhn R, Trieschmann H (1964) Monatsh Chem 95:457
14. Braun D, Czerwinski WK (1987) Makromol Chem 188:2371
15. Greenley RZ (1980) J Macromol Sci, Chem A14:427
16. Larina GN, Borisova ZV, Sheremeteva TV (1961) Vysokomol Soed 3:1664
17. Bai F, Chang CH, Webber SE (1986) Am Chem Soc, Div Polym Chem, Polym Prepr 27:327

Authors' address:

Prof. Dr. D. Braun
Deutsches Kunststoff-Institut
Schloßgartenstr. 6
D-6100 Darmstadt, F.R.G.