**Journal of Macromolecular Science, Part A**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

# The Copolymerization of Alkenes with Maleic Anhydride

M. Rätzsch[a]
[a] Institute of Polymer Technology Academy of Sciences of the GDR, Dresden, German Democratic Republic

**To cite this Article** Rätzsch, M.(1987) 'The Copolymerization of Alkenes with Maleic Anhydride', Journal of Macromolecular Science, Part A, 24: 5, 517 — 526
**To link to this Article: DOI:** 10.1080/00222338708068138
**URL:** http://dx.doi.org/10.1080/00222338708068138

J. MACROMOL. SCI.–CHEM., A24(5), pp. 517-526 (1987)

# THE COPOLYMERIZATION OF ALKENES WITH MALEIC ANHYDRIDE

M. RÄTZSCH
Institute of Polymer Technology
Academy of Sciences of the GDR
8010 Dresden, German Democratic Republic

## ABSTRACT

The investigations presented deal with the experimental results of the copolymerization of maleic anhydride (MAn) with alkenes. The course of the reaction is explained by the overall rate of the copolymerization ($\nu_{Br}$), which correlates with the solution viscosity of the copolymer, and the dependence of the $\nu_{Br}$ maximum on the mole ratio of the monomers at constant total monomer concentration. The use of solvents with increasing donor power leads to increased complexing of the free MAn molecules and of the MAn radical chain ends. The results demonstrate that, for low 1-alkenes, the addition of the MAn chain radical is the rate-determining step of the copolymerization. As the substituents on the olefinic double bond become larger or the double bond shifts to the 1,2-position, the addition of MAn to the hydrocarbon radical becomes more and more the rate-determining step. On the other hand, an increase of the CT complexation of the MAn polymer radical by use of donor solvents decreases the alkene addition rate.

## INTRODUCTION

Our investigation started with the results of our work in 1975 on the copolymerization of cyclopentene (CP), norbornene (NB), and dihydrodicyclopentadiene (DHDCP) with MAn. These results were not published because of difficulty in interpretation. Our more recent investigations and the increased understanding of these copolymerizations have made it possible to include the former results and to interpret them. The interpretation gives the dependence of the polymerization rate ($\nu_{Br}$) on the nature of the solvent and that of the position of the maximum of $\nu_{Br}$ on the monomer concentration ratio at constant total concentration.

## EXPERIMENT

The copolymerization was performed under nearly complete exclusion of oxygen since oxygen effects have been shown to be significant in the case of the copolymerization of styrene with MAn [1]. The polymerization experiments were performed in a special dilatometer with mercury as sealing fluid, the manipulation having been described previously [2].

MAn was purified by distillation under inert gas and subsequent sublimation in vacuo. Hydrolysis of MAn was avoided by this method since the influence of maleic acid on the copolymerization rate has been demonstrated [3]. Before use, the alkenes were distilled over sodium under inert gas. The solvents dichloroethane (DCE), acetone (AC), and cyclohexanone (CH) were dried over calcium hydride and $P_2O_5$, respectively, and then fractionated.

The conditions of the copolymerization are shown in the corresponding figures and tables. The resulting copolymers were precipitated with isopropanol or in *n*-heptane at about -20°C, treated repeatedly with dry *n*-heptane, and dried at 50°C to constant weight in vacuo.

## EXPERIMENTAL RESULTS

In Table 1, relative copolymerization rates $\nu_{Br}$ are shown for constant reaction conditions for the copolymerization of MAn with CP, NB, and DHDCP in different solvents. These results show (Fig. 1) a linear dependence of $\nu_{Br}$ on the donor power (DP) of the solvent, whereas there is no influence of the dielectric constant (DC) of the solvent (Fig. 1). Table 2 shows that the activation energies ($E_A$) rise with increasing DP of the solvent and decreasing $\nu_{Br}$.

Figures 2 to 4 show the overall polymerization rates of CP, NB, and DHDCP in toluene, dioxane, and methyl ethyl ketone (MEK) as functions of the monomer ratio at constant total monomer concentration. A shift of the $\nu_{Br}$ maximum can definitely be recognized when going from CP to DHDCP. Accordingly, it can be concluded that, for every monomer, the

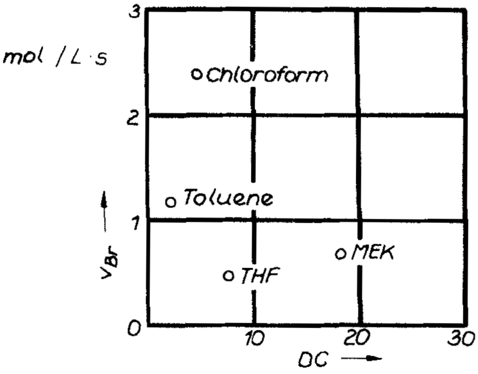
TABLE 1. Dependence of the Polymerization Rate on the Donor Power (DP) of the Solvent

| | | $\nu_{Br}$, %/min | | |
|---|---|---|---|---|
| Solvent | DP | CP/MAn | NB/MAn | DHDCP/MAn |
| Chloroform | 0 | 0.283 | 0.101 | 0.023 |
| Toluene | 10 | 0.173 | 0.056 | 0.005 |
| Dioxane | ~15 | 0.10 | 0.052 | [a] |
| Methyl ethyl ketone | 17 | 0.079 | 0.049 | 0.004 |
| Tetrahydrofuran | 20 | 0.016 | Traces | Traces |
| Dimethylformamide | 26.6 | – | – | – |

[a] Not performed.

absolute value of $\nu_{Br}$ decreases and its maximum shifts to lower MAn concentrations with increasing DP of the solvent. To confirm this result, detailed investigations were performed of the copolymerization of MAn with ethylene (Et), propylene (Pr), isobutene (IB), 4-methylpentene-1 (4-MP-1), 2,4,4-trimethylpentene-1 (2,4,4-TMP-1), 2,4,4-trimethylpentene-2 (2,4,4-TMP-2), and, for comparison purposes, with styrene (St) and isobutyl vinyl ether (IBVE). Figure 5 shows the change in $\nu_{Br}$ during the copolymerization of MAn with Pr, IB, St, and IBVE at a constant total monomer concentration in DCE. Except with Pr, all $\nu_{Br}$ maxima are at a mole ratio of about 0.5. The high $\nu_{Br}$ of IB, which lies above that of St and IBVE, is surprising.

Table 3 shows the $\nu_{Br}$ values of the solution copolymerization of the different alkenes at the maximum, the position of the maximum, and the reduced viscosities as relative measures of the molecular weights. Again, the high $\nu_{Br}$ and the corresponding high reduced viscosity of the IB/MAn copolymer are striking. Insignificant deviations of $\nu_{Br}$ and reduced viscosity are shown by 2,4,4-TMP-1. Apart from these deviations, both $\nu_{Br}$ and the reduced viscosity decrease with increasing steric hindrance of the alkene. The maximum of the $\nu_{Br}$ curves shifts with increasing steric hindrance of the alkenes from the alkene excess range to the MAn excess range. In solvents with higher DP, as, for example, acetone (AC) for 2,4,4-TMP-1 and cyclohexanone for IB, the direction of the shift changes. These results correspond to the results of the copolymerization of MAn with CP, NB, and DHDCP, as discussed above.



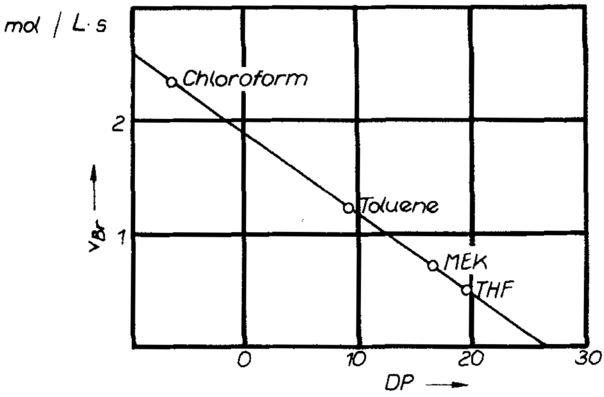


FIG. 1. Dependence of the relative copolymerization rates $\nu_{Br}$ in solution on the dielectric constant (upper figure) and on the donor power (lower figure) of the solvent.

## DISCUSSION

We interpret the variation of $\nu_{Br}$ on the donor power (DP) of the solvent in Fig. 1 as due to charge-transfer (CT) complexation of the MAn radical chain ends by the solvent, which increases with the DP of the solvent. The influence of the complexation of the free MAn by the solvent on $\nu_{Br}$ is, indeed, not separable from the influence of the complexation of the MAn chain end, but

TABLE 2. Dependence of the Relative Overall Rate of the Copolymerization of Cyclopentene with MAn ($\nu_{\mathrm{Br}}$) and the Activation Energy ($E_A$) on the Donor Power (DP) of the Solvents

| Solvent | DP | $E_A$, kcal/mol | $\nu_{\mathrm{Br}}$, %/min |
|---|---|---|---|
| Chloroform | 0 | 12.5 | 0.28 |
| Toluene | 10 | 14.0 | 0.17 |
| Dioxane | 15 | 19.0 | 0.10 |
| Methyl ethyl ketone | 17 | 20.5 | 0.08 |
| Tetrahydrofuran | 20 | 22.0 | 0.02 |

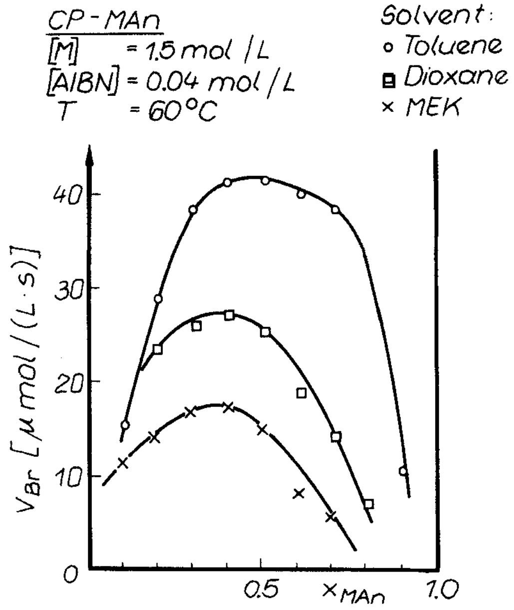


FIG. 2. Dependence of the overall copolymerization rates $\nu_{\mathrm{Br}}$ of cyclopentene (CP) on the monomer composition at constant total monomer concentration in toluene, dioxane, and methyl ethyl ketone (MEK).

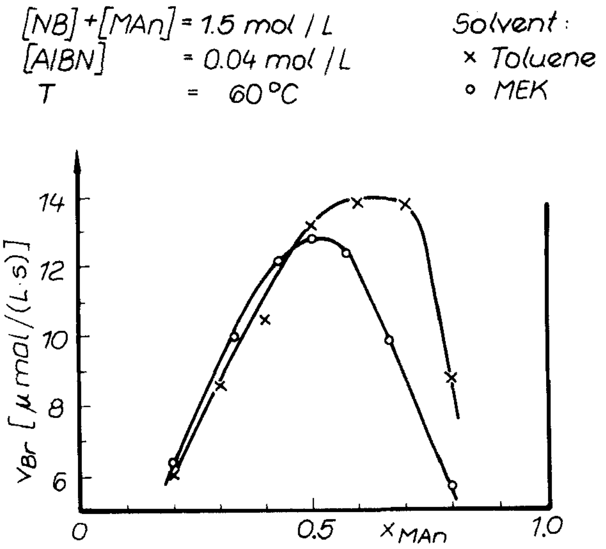


FIG. 3. Dependence of the overall copolymerization rates $\nu_{Br}$ of norbornene (NB) on the monomer composition at constant total monomer concentration in toluene and methyl ethyl ketone (MEK).

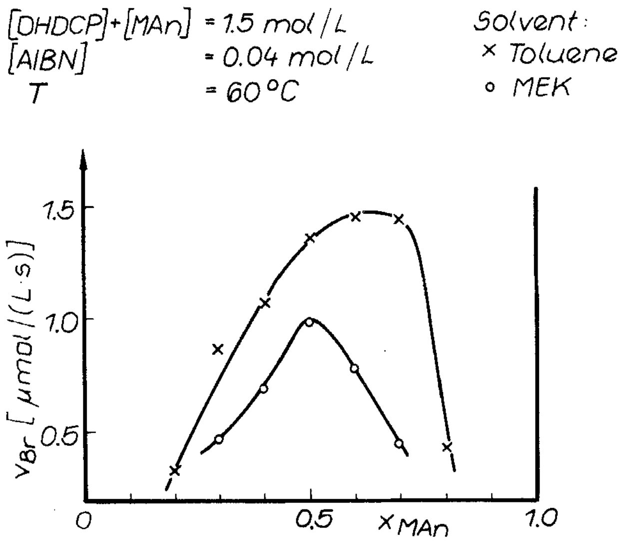


FIG. 4. Dependence of the overall copolymerization rates $\nu_{Br}$ of dihydrodicyclopentadiene (DHDCP) on the monomer composition at constant total monomer concentration in toluene and methyl ethyl ketone (MEK).

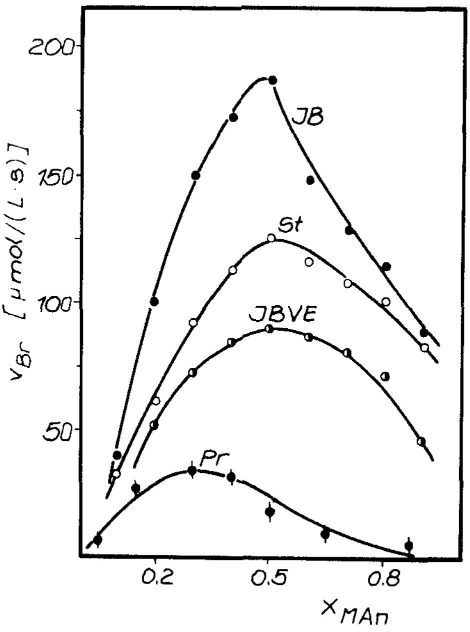


FIG. 5. Dependence of the overall copolymerization rates of isobutene (IB), styrene (St), isobutyl vinyl ether (IBVE), and propene (Pr) on the monomer composition at constant total monomer concentration in dichloroethane (DCE) as solvent. [Monomer] + [MAn] = 1.5 mol/L; [AIBN] = 1 mmol/L; solvent, DCE; 60°C.

leads merely to a lowering of the free monomer concentration. However, the correlation between DP and $E_A$ indicates hindrance of addition to the MAn radical chain end because of the complexation by the solvent and cannot be explained by a lowering of the free MAn concentration.

The decrease of $\nu_{Br}$ from CP to DHDCP, as shown in Table 1, comes from the increasing steric hindrance during the monomer addition. Knowledge of $\nu_{Br}$ and $E_A$ is insufficient to decide which of the two addition steps is hindered. An analogous dependence is given in Table 3 for the alkenes Et, Pr, 4-MP-1, 2,4,4-TMP-1, and 2,4,4-TMP-2 [4]. The strong deviations for IB and the smaller ones for 2,4,4-TMP-1 in DCE cannot be due only to their high reactivity because of their high $e$ values (from the $Q,e$ scheme, $e$ = -0.96 for IB

TABLE 3. Solution Polymerization of Alkenes with MAn[a]

| Comonomer | $\nu_{Br}$, $\mu$mol/(L·s) | $\nu_{Br\ max}$, $x_{MAn}$[b] | $\eta_{sp}/c$, dL/g |
|---|---|---|---|
| Et[c] | 3000 | 0.2 | |
| Pr | 380 | 0.3 | 0.6 |
| IB | 3700 | 0.5 | 16 |
| IB[d] | 600-800[e] | 0.4 | ~10[e] |
| 4-MP-1 | 28-30 | 0.5 | 0.22 |
| 2,4,4-TMP-1 | 30 | 0.8 | 0.8 |
| 2,4,4-TMP-2 | 6.2 | 0.7 | 0.22 |
| 2,4,4-TMP-2[c] | 4.1 | 0.6 | 0.20 |

[a] Solvent: DCE; [M] = 3 mol/L; $T$ = 323 K; [I] = 0.01 mol/L.

[b] Mole fraction MAn.

[c] In acetone.

[d] In cyclohexanone.

[e] Recalculated from measurements with [I] = 1 mmol/L. Obtained values: $\nu_{Br}$ = 250 $\mu$mol/L·s and $\eta_{sp}/c$ = 7.0 dL/g (on the basis of [I] = 10 mmol/L).

and $e = -1.77$ for 2,4,4-TMP-1). The assumption of a distinctly reduced termination rate by steric hindrance explains this [5].

The reduced viscosities correlate with the $\nu_{Br}$ values and also confirm their course for the deviations with IB and 2,4,4-TMP-1. This demonstrates that the relative change of the molecular weight is determined essentially by the propagation reaction. The $\nu_{Br}$ maxima show that addition of the low alkenes to the MAn chain radical is the rate-determining step (Fig. 6).

Enlargement of the substituents at the double bond of the alkene causes the $\nu_{Br}$ maximum to shifts to higher MAn concentrations because of steric hindrance in the MAn addition to the olefinic radical chain end. The addition rate of the alkenes decreases, moreover, because of the increasing steric hindrance or of the 1,2-substitution but not to such an extent that the $\nu_{Br}$ maximum can be shifted in the direction of increased MAn concentration. However, by comparison, the complexation of the MAn radical chain end with a donor solvent (AC, CH, MEK, THF) causes a shift of the $\nu_{Br}$ maximum in the

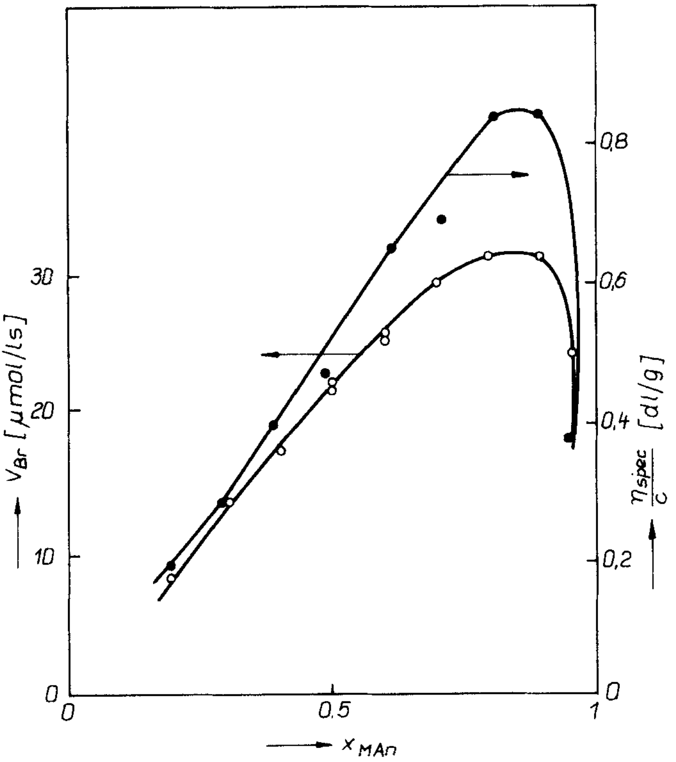


FIG. 6. Dependence of the overall copolymerization rates, and of the reduced viscosities ($\eta_{sp}/c$) of 2,4,4-trimethylpentene-1/MAn on the monomer composition at constant total monomer concentration in dichloroethane as solvent. [TMP-1] + [MAn] = 1.5 mol/L; [AIBN] = 10 mmol/L; 50°C.

direction of higher alkene concentrations, i.e., a lowering of the alkene addition rate. This dependence is overlapped by the electron-donating effect (*e* value) of the alkenes.

## CONCLUSIONS

An overall interpretation is the assumption of a separate addition step of the monomers.

Second, the addition steps of the alkenes can be described in terms of the difference between the $e$ values of the radical chain end and the alkene. The CT complexation of solvent and monomer with the MAn radical chain end diminishes this difference apart from the geometrical nature of the substituents (especially 1,1- and 1,2-substituents).

Third, the rate of MAn addition to the radical chain end of the alkene is influenced appreciably by steric factors. These results are in accordance with our earlier results describing the mechanism of the radical copolymerization of MAn with donor monomers [6].

## REFERENCES

[1] M. Arnold, *Plaste Kautsch.*, *27*, 10 (1980).
[2] M. Rätzsch, G. Schicht, and M. Arnold, *Acta Polym.*, *33*, 433 (1982).
[3] M. Rätzsch, V. Steinert, J. Rochner, and M. Arnold, *Plaste Kautsch.*, *31*, 165 (1984).
[4] M. Rätzsch, M. Arnold, and V. Steinert, *Acta Polym.*, *36*, 8 (1985).
[5] M. Rätzsch and M. Arnold, *Makromol. Chem.*, To Be Published.
[6] M. Rätzsch and V. Steinert, *Ibid.*, *185*, 2411 (1984).

Received January 9, 1986
Revision received June 2, 1986