Vinyl Polymerization. 259. Polymerization of Methyl Methacrylate Initiated by p-Methoxy-p'-cyanodiphenyldiazomethane

Tadao Nakaya[a]; Hiroshi Wada[a]; Minoru Imoto[a]

[a] Osaka City University Faculty of Engineering Sugimoro-cho, Sumiyoshi-ku, Osaka, Japan

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Vinyl Polymerization. 259. Polymerization of Methyl Methacrylate Initiated by p-Methoxy-p'-cyanodiphenyldiazomethane

TADAO NAKAYA, HIROSHI WADA, and MINORU IMOTO

Osaka City University
Faculty of Engineering
Sugimoro-cho, Sumiyoshi-ku
Osaka, Japan

SUMMARY

A study of the polymerization of methyl methacrylate (MMA) in benzene initiated by p-methoxy-p'-cyanodiphenyldiazomethane (MCD) was made. The initial rate of the polymerization, R_p, followed the equation:

$$R_p = k[MCD]^{0.56}[MMA]^{0.95}$$

The rate for decomposition of MCD was measured in benzene in the range 50 to 80°C, and the following rate equation was obtained:

$$k_d[sec^{-1}] \approx 7.42 \times 10^{12} \exp(-25.7 \text{ kcal}/RT)$$

On the basis of the results, the initiation mechanism of the polymerization by MCD is discussed.

INTRODUCTION

In the previous paper [1], the polymerization of methyl methacrylate

(MMA) initiated by diphenyldiazomethane (DDM) was investigated. In the present paper, we describe the results of detailed kinetic and mechanistic studies on the polymerization of MMA initiated by p-methoxy-p'-cyanodiphenyldiazomethane (MCD), bearing an electron-donating and an electron-withdrawing substituents at both para positions of the benzene rings of DDM. The effect of substituents on the reactivity of an initiator is also discussed.

<div align="center">

EXPERIMENTAL

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Preparation of p-Methoxy-p'-cyanodiphenyldiazomethane (MCD)

MCD was prepared by the following scheme:

(MCB)

(MCBH)

(MCD)
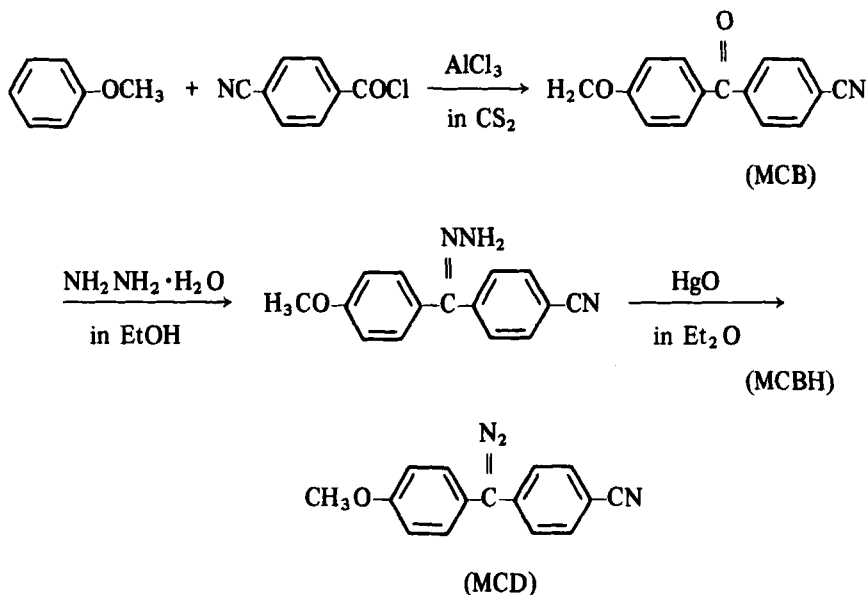
p-Methoxy-p'-cyanobenzophenone (MCB)

In a three-necked flask, fitted with a mechanical stirrer and a reflux condenser and protected with a calcium chloride tube, were placed 10 g of 4-cyanobenzoyl chloride, 10 g of anisole, and 70 ml of carbon disulfide. To the ice-cold and well-stirred mixture was added 14 g of aluminum chloride. After the addition, the mixture was allowed to stand at room

temperature for 1 hr and was then heated at 40°C for 4 hr. The mixture was cooled in an ice bath under stirring, and then hydrolyzed by pouring into the mixture of hydrochloric acid and cracked ice. After the aqueous layer was separated out, the solvent was removed by distillation under reduced pressure. The residue was recrystallized from ethanol giving 4.3 g (30%) of MCB as colorless crystals, mp 134-135°C; IR(KBr) 1635 cm^{-1} (C=O), 2200 cm^{-1} (C≡N), 2850, 2950, 2990, and 3080 cm^{-1} (OCH$_3$).

Analysis calculated for C$_{15}$H$_{11}$O$_2$N: C, 75.97; H, 4.64; N, 5.90. Found: C, 76.11; H, 4.98; N, 5.80.

p-Methoxy-p'-cyanobenzophenone Hydrazone (MCBH)

A mixture of 1 g of MCB and 1 g of 80% hydrazine hydrate in 15 ml of absolute ethanol was refluxed for 10 hr. After cooling in an ice bath, the solid material that separated was collected by filtration and dried under vacuo. Recrystallization from ethanol gave MCBH as colorless needles, melting at 154-155°C, in a 85% yield. IR (KBr) 2200 cm^{-1} (C≡N), 2830, 2950, 3000, and 3070 cm^{-1} (OCH$_3$).

Analysis calculated for C$_{15}$H$_{13}$ON$_3$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.91; H, 5.07; N, 16.83.

p-Methoxy-p'-cyanodiphenyldiazomethane (MCD)

A mixture of 3 g of MCBH, 7.5 g of anhydrous sodium sulfate, 3 g of yellow mercuric oxide, 150 ml of ethyl ether, and 3 ml of ethanol saturated with potassium hydroxide was stirred under nitrogen at room temperature. The reaction mixture was then filtered through a glass filter. When the filtrate was concentrated under reduced pressure, red crystals with mp 86°C were obtained in 82% yield.

Analysis calculated for C$_{15}$H$_{11}$ON$_3$: C, 72.27; H, 4.45; N, 16.86. Found: C, 71.95; H, 4.31; N, 16.33.

The Reaction of MCD with Methyl Methacrylate (MMA)

A mixture of 3 g of MCD and 15 g of MMA in 100 ml of ethyl ether was allowed to stand for 2 days at room temperature until the purple-red color disappeared. The solvent and the excess of MMA were distilled out in vacuo and the solid material obtained was dissolved in 50 ml of methanol. The methanol solution was filtered off to exclude the contaminated polymeric materials. The filtrate was evaporated under reduced

pressure to separate the white crystals. Recrystallization from methanol gave methyl-1-methyl-2-(p-methoxyphenyl)-2-(p'-cyanophenyl)-cyclopropyl-carboxylate, mp 120°C, in 0.9 g yield. The NMR spectrum showed the absorptions at 1.2 ppm (three protons) for methyl protons, 1.2-1.5 and 2.2-2.3 ppm (two protons) for methylene protons, 3.4 ppm (three protons) for the methoxy protons, 3.7 ppm (three protons) for the carbomethoxy protons, and 6.8-7.9 ppm (eight protons) for the phenyl protons.

Analysis calculated for $C_{20}H_{19}O_3N$: C, 74.75; H, 5.96. Found: C, 74.47: H, 5.92.

Measurement of the Rates of Decomposition of MCD and Diphenyldiazomethane (DDM)

The benzene solution, in which the initial concentration of MCD was adjusted to 1.0×10^{-2} mole/liter, was quickly placed in an ampoule, cooled in a Dry Ice-methanol bath, and sealed in vacuum. The sealed ampoule was shaken in a thermostat maintained at a definite temperature. Thermal decomposition proceeded. After a definite time, the decrease in the absorbance of the solution at 517 mμ (ϵ = 110) was followed by Hitachi Model EPS-2U recording spectrophotometer.

The rate of thermal decomposition of DDM in benzene was measured at 527 mμ (ϵ = 131) by the same procedure as described above.

Polymerization

MMA and styrene were purified by the usual method and distilled under reduced pressure three times in a stream of nitrogen before use. Benzene was purified by the usual method.

The polymerization procedure was the same as that in the previous paper [1].

Degree of Polymerization

Number-average degree of polymerization, P_n, of polymethyl methacrylate was calculated according to the following Schuele's equation [2].

$$P_n = 2.22 \times 10^3 [\eta]_0^{1/0.76} \quad \text{(in benzene at 30°C)} \quad (1)$$

RESULTS

The Rate of Thermal Decomposition

The rate of the thermal decomposition of MCD in benzene was estimated by measuring the rate of the disappearance of the characteristic peak at 517 mμ (ϵ = 110), due to absorption by the diazo group of MCD.

For DDM, the kinetics was studied by the absorption at 527 mμ (ϵ = 131) by the same procedure as that used for MCD. The first-order rate constants for MCD and DDM at 50, 60, 70, and 80°C are listed in Table 1.

Table 1. The Rate of the Decomposition
of MCD and DDM in Benzene

Compound	Temperature (°C)	$k_d \times 10^4$ (sec^{-1})
MCD	50	0.30
	60	1.05
	70	4.78
	80	9.08
DDM	60	0.20
	70	0.30
	80	1.31
	90	3.72

Arrhenius plots of the Table 1 data gave good straight lines, as shown in Fig. 1, from which the following first-order rate constants were obtained:

$$k_d \text{ (sec}^{-1}) = 0.74 \times 10^{13} \exp (-25.7 \text{ kcal/RT}) \quad (MCD) \quad (2)$$

$$k_d \text{ (sec}^{-1}) = 1.32 \times 10^{13} \exp (-27.5 \text{ kcal/RT}) \quad (DDM) \quad (3)$$

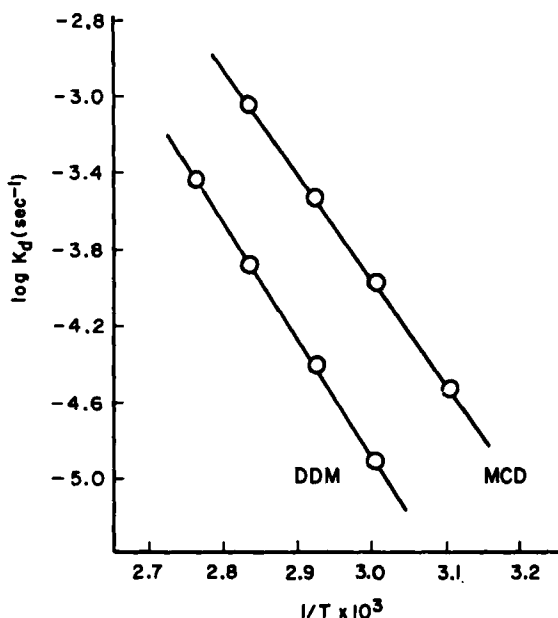The difference in the activation energies for decomposition between MCD and DDM is relatively small.

Fig. 1. Arrhenius plots for decomposition of MCD and DDM.

Activation Energy of the Polymerization of MMA with MCD

The polymerization of MMA with MCD was carried out in benzene from 40 to 70°C. Figure 2 shows the time conversion curves of the polymerization.

The over-all activation energy of the polymerization was calculated as 15.3 kcal/mole from the Arrhenius plot of the rates of polymerization measured between 40 and 70°C, as shown in Fig. 3.

On the other hand, the over-all activation energy of the polymerization of MMA in benzene with DDM was estimated as 18.8 kcal/mole from the rates at 50, 60, 70, and 80°C. It should be noted that the over-all activation energy of the polymerization of MMA with DDM in the absence of solvent was 13.1 kcal/mole [1].

Confirmation of a Radical Mechanism of the Polymerization with MCD

Hydroquinone inhibited the polymerization of MMA initiated by MCD. Moreover, a copolymerization of MMA with styrene (St) was carried out in bulk at 50°C. Figure 4 shows the composition curve which is
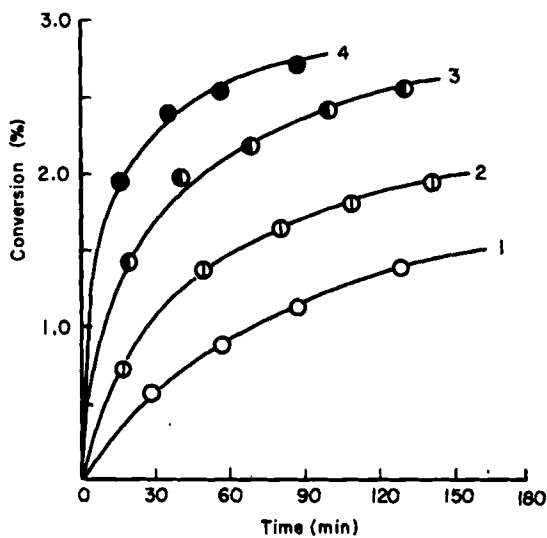
Fig. 2. Conversion vs. time in the polymerization of MMA initiated by MCD. [MMA] = 4.68 moles/liter, [MCD] = 3.00 $\times$ 10^{-2} moles/liter. Curve 1: 40°C; 2: 50°C; 3: 60°C; 4: 70°C.
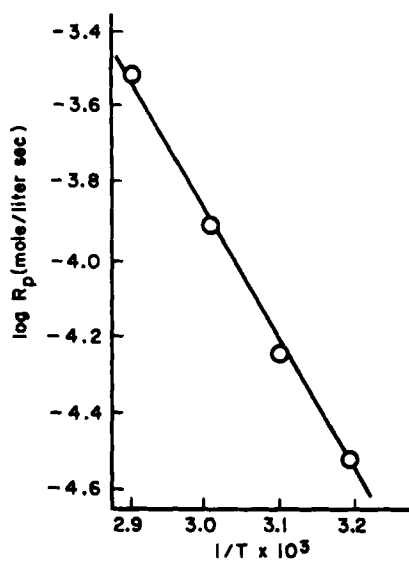

Fig. 3. Relationship between R_p and polymerization temperature.

characteristic of radical copolymerization, of the copolymers obtained. It was, therefore concluded that the polymerization of MMA with MCD proceeded through a radical mechanism.
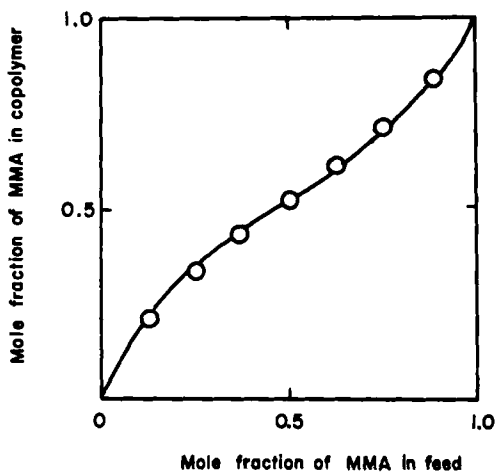

Fig. 4. Composition curve for the bulk copolymerization of MMA with with styrene at 50°C. [MCD] = 3×10^{-2} moles/liter.

Table 2. Results of the Polymerization of MMA Initiated by MCD in Benzene at 50°C

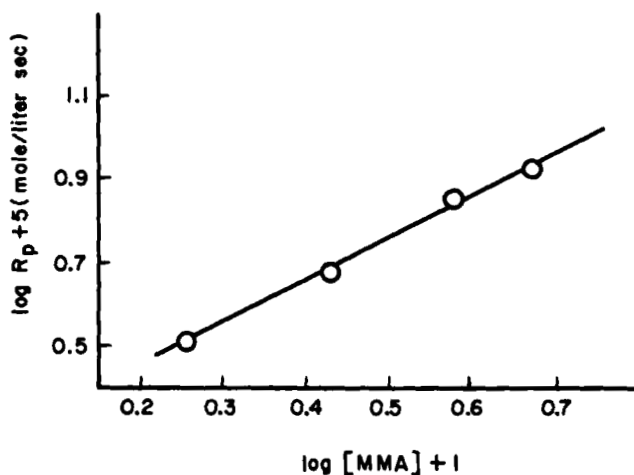| [MMA] (moles/liter)	[MCD] (moles/liter)	$R_p \times 10^5$ (moles/liter sec)	$P_n \times 10^{-3}$
4.68	1.50	3.90	10.5
4.68	3.00	5.20	5.9
4.68	4.50	6.24	4.4
4.68	6.00	7.80	3.8
4.68	9.00	9.36	3.0
4.68	5.00	8.06	—
3.74	5.00	7.02	—
2.67	5.00	4.68	—
1.79	5.00	3.22	—

Fig. 5. Relationship between R_p and the concentration of MMA (in benzene at 50°C).
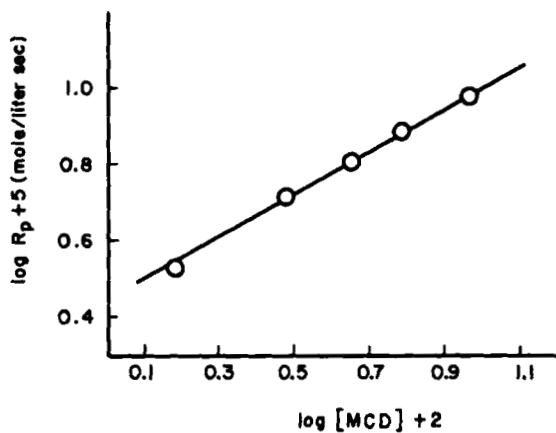

Fig. 6. Relationship between R_p and the concentration of MCD (in benzene at 50°C).

Rate of the Polymerization of MMA with MCD

The polymerization of MMA with MCD was carried out in benzene at 50°C. The conditions employed and the results obtained are summarized

in Table 2. Figures 5 and 6 illustrate the plots of the data given in Table 2.

From Figs. 5 and 6 it was concluded that the initial rate of the polymerization, R_p, is proportional to the 0.56 power of the concentration of MCD and to the 0.95 power of that of MMA. Thus, we obtain

$$R_p = k[MCD]^{0.56}[MMA]^{0.95} \qquad\qquad (5)$$

The rate Eq. (4) agreed very well with Eq. (5).

The number-average degrees of polymerization, P_n, of the polymer obtained by the polymerization in benzene at 50°C, where [MMA] and [MCD] were 0.179 mole/liter and 5.0×10^{-2} moles/liter, respectively, were measured.

Table 3. Relationship between P_n and the
Duration of the Polymerization Time of MMA
at 50°C in Benzene with MCD as Initiator:
[MMA] = 0.179 mole/liter,
[MCD] = 5.0×10^{-2} moles/liter

Time (min)	Conversion (%)	$P_n \times 10^{-3}$
30	0.68	1.32
60	1.08	1.55
105	1.71	1.75
150	2.28	1.97

From Table 3 it is apparent that the degree of polymerization of the polymers increased with the polymerization time [3, 4].

The result was different from that obtained by the polymerization with DDM [1], where P_n was almost constant during the polymerization.

DISCUSSION

As mentioned above, it is apparent that the polymerization of MMA
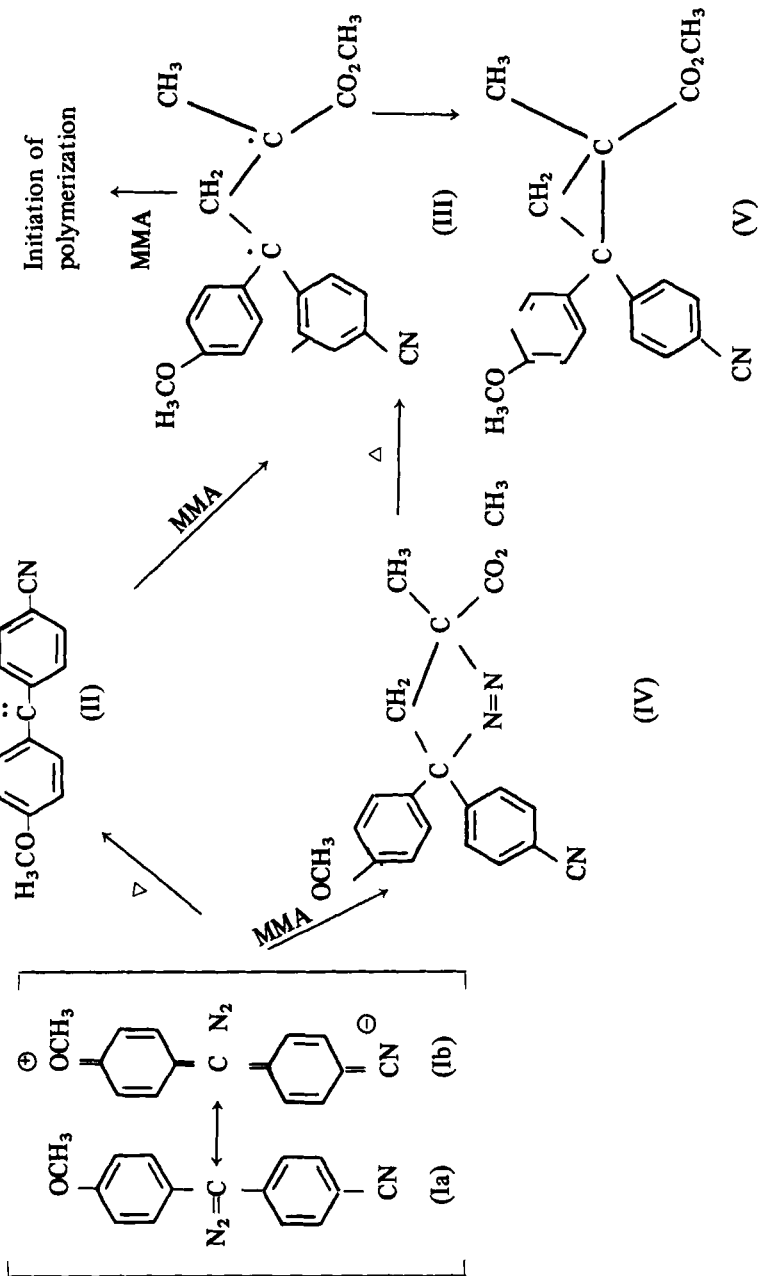
initiated by MCD proceeded through a free radical mechanism. Using the radical mechanism, two different reaction pathways may be proposed [5-8]. These are summarized in the scheme shown on the preceding page.

One path involves, in the first step, the loss of nitrogen and formation of a carbene intermediate (II) by thermal decomposition of the diazo compound (I). This carbene may react with MMA to give the diradical intermediate (III), leading to a cyclopropane derivative (V) as the major product and to an initiator as the minor product [1]. The alternative possibility is that the diazo compound (I) may add to MMA with formation of a pyrazoline ring (IV) which, on thermal decomposition, gives rise to the diradical intermediate as described above. However, the observation that the rate of polymerization is proportional to the 0.56 power of [MCD] and the 0.95 power of [MMA] is favorable to the first route which involves a carbene intermediate rather than the second route which involves a pyrazoline intermediate. From the over-all activation energy obtained here, the activation energy of initiation, E_i, was estimated to be 22.6 ± 2 kcal/mole by the following equation, using the value of $E_p - \frac{1}{2}E_t = 4\sim5$ kcal/mole, given by Tobolosky et al. [9].

$$E = E_p + \frac{1}{2}E_i - \frac{1}{2}E_t \qquad (6)$$

The E_i value calculated here is close to that of the activation energy of decomposition for MCD.

The finding that the activation energy for decomposition of MCD is lower than that of DDM suggests that the methoxy and cyano substituents at both para positions on DDM promote the decomposition of MCD by the resonance interaction involving Structure Ib. The rate equation presented here is in agreement with that previously obtained by using DDM as initiator. Furthermore, the over-all activation energy of polymerization of MMA initiated by MCD is close to that obtained by using DDM as initiator. From these results, it can be said that the polymerization of MMA initiated by MCD is analogous to that obtained by DDM, regardless of the introduction of the polar groups.

REFERENCES

[1] T. Nakaya, K. Ohashi, and M. Imoto, *Makromol. Chem.*, 114, 201 (1968).

[2] Cf. J. L. O'Brien and F. Gornick, *J. Amer. Chem. Soc.*, **77**, 4559 (1955).
[3] M. Imoto, T. Nakaya, T. Tomomoto, and K. Ohashi, *J. Polym. Sci., Part B*, **4**, 955 (1966).
[4] T. Nakaya, K. Ohashi, and M. Imoto, *Makromol. Chem.*, **111**, 115 (1968).
[5] W. Kirmse, *Carbene Chemistry*, Academic, London, 1964, p. 97.
[6] G. W. Cowell and A. Ledwith, *Quart. Rev.* (London), **24**, 119 (1970).
[7] R. Huisgen, H. Stangel, H. J. Sturm, and H. Wagenhofer, *Angew. Chem.*, **73**, 170 (1961).
[8] A. Ledwith and D. Parry, *J. Chem. Soc., B*, **1966**, 1408.
[9] T. E. Fering and A. V. Tobolsky, *J. Colloid Sci.*, **12**, 325 (1957).