

The Free Radical Polymerization of N,N-Dimethylacrylamide

A. M. NORTH and A. M. SCALLAN

The free radical homopolymerization and copolymerization of N,N-dimethylacrylamide has been investigated at 50°C. Individual rate constants have been obtained for all the relevant propagation, transfer, and termination processes. The high propagation rate constant is due to the abnormal reactivity of the free radical rather than the monomer.

ALTHOUGH detailed studies^{1,2} of the solution polymerization of acrylamide have been made, no values have yet been reported for the rate constants of the polymerization of *N,N*-dialkylacrylamides. In this publication are reported conventional studies of the free radical homopolymerization and copolymerization of *N,N*-dimethylacrylamide.

EXPERIMENTAL

Materials

N,N-dimethylacrylamide was kindly supplied by British Nylon Spinners.

The monomer was dried over freshly ground calcium hydride, and fractionally distilled on the vacuum line at 30°C. Traces of inhibitor which co-distilled with the monomer were removed by prepolymerizing to 20 per cent conversion, the residual monomer being distilled directly into the reaction vessel.

Methylmethacrylate, B.D.H. purified grade, was freed of inhibitor and distilled under a nitrogen pressure of 20 mm of mercury. The middle fraction was collected, and aliquot portions outgassed on the vacuum line at pressures less than 5×10^{-5} mm of mercury, prepolymerized by ultra-violet irradiation, and residual monomer distilled into the polymerization vessels.

Styrene was treated in the same way as methylmethacrylate.

Toluene, analytical reagent grade, was dried by refluxing over sodium. In one series of experiments sulphur compounds were removed by refluxing with mercuric acetate solution. However, kinetic experiments using toluene so treated were identical with those carried out using untreated toluene, and the procedure was dispensed with in later experiments.

α,α' -Azobisisobutyronitrile (AZBN) was recrystallized three times from ethanol and stored in the dark at -10°C .

Procedure

Rates of polymerization were observed using conventional dilatometers, immersed in a water thermostat bath governed to $50^\circ \pm 0.01^\circ\text{C}$. The meniscus movement was observed using a cathetometer reading to ± 0.001 cm.

Molecular weights were determined from intrinsic viscosities (measured in an Ubbelohde suspended level viscometer) using the relationship of

Trossarelli and Meirone³. Instantaneous number average molecular weights were calculated from weight average values measured on whole polymer samples (polymerization being carried to a finite monomer-polymer conversion) using the equation derived by Schultz⁴.

The rotating sector was constructed from brass with two apertures capable of variation from 0° to 90° segmental angle. The sector was driven by a Jones and Stevens [Type R.Z.G.] induction motor with a continuously variable gear box. The sector was arranged so as to chop the light beam at its focal point.

All measurements of polymerization rate were carried out below five per cent conversion monomer to polymer.

Copolymer compositions were determined by microanalysis of the nitrogen content.

RESULTS

The contraction-conversion factor

Seventeen polymerizations were carried out in which the resulting polymer was weighed, and the fractional conversion so obtained compared with the contraction observed. The average value of the percentage volume contraction corresponding to 100 per cent conversion was obtained as 16.9 (standard deviation 1.3).

Rates of homopolymerization

The dependences of the rate of polymerization upon the concentrations of monomer and of initiator (AZBN) are illustrated in *Figures 1* and *2*. The polymerization rate is proportional to the first power of the monomer concentration and the square root of the initiator concentration only at high monomer and low initiator concentrations.

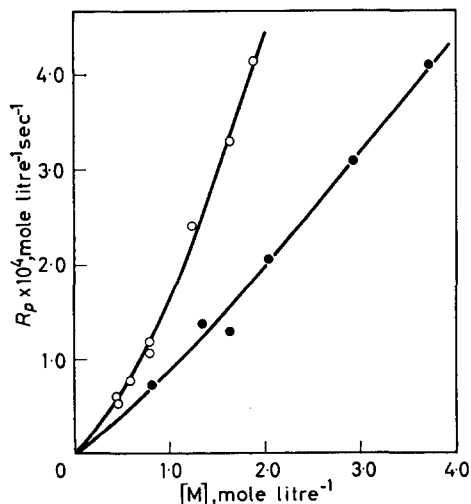


Figure 1—Rate of polymerization against monomer concentration.
 ○ [Init.] 1.32×10^{-2} mole litre⁻¹;
 ● [Init.] 2.17×10^{-3} mole litre⁻¹

Figure 2—Rate of polymerization against square root α,α' -azoisobutyronitrile concentration; $[M]$ 0.81 mole litre⁻¹. ○ Experimental points. Unbroken line represents curve calculated assuming primary radical combination

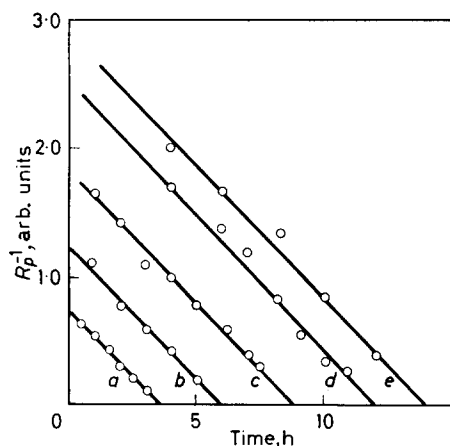
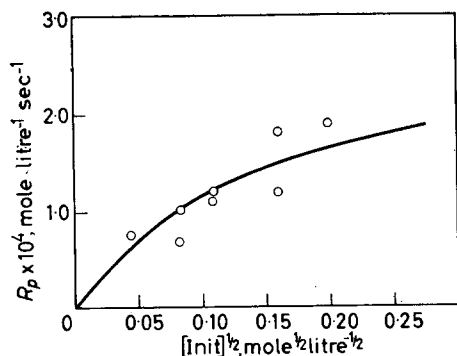


Figure 3—Determination of inhibition periods. $[Init.]$, 4.0×10^{-2} mole litre⁻¹. Benzoquinone concentrations: a, 1.3×10^{-3} ; b, 3.5×10^{-3} ; c, 1.6×10^{-3} ; d, 2.4×10^{-3} ; e, 3.5×10^{-3} (all mole litre⁻¹). Monomer concentrations: a, 8.1×10^{-1} ; b, 4.1×10^{-1} ; c, 8.1×10^{-1} ; d, 4.1×10^{-1} ; e, 8.1×10^{-1} (all mole litre⁻¹)

Rates of initiation were calculated from inhibition times using the kinetic analysis of Burnett and Cowley⁵. Benzoquinone was used as inhibitor, and plots of reciprocal rate of polymerization against time are illustrated in Figure 3. Comparison of the rates of initiation so obtained with literature values for the rate of decomposition of AZBN⁶ yields an initiator efficiency in this system of 0.38.

When the rate of initiation is compared with the rate of polymerization at high monomer and low catalyst concentrations it is possible to obtain the ratio

$$k_p / (2k_{tc} + 2k_{td})^{1/2} = R_p / [M] R_i^{1/2} \quad (1)$$

where k_p , k_{tc} , k_{td} are the rate constants for propagation, termination by combination and termination by disproportionation respectively. At 50°C the ratio had the value,

$$k_p / (2k_{tc} + 2k_{td})^{1/2} = 1.78 \text{ litre}^{1/2} \text{ mole}^{-1/2} \text{ sec}^{-1/2}$$

Degrees of polymerization

It was found that the measured degrees of polymerization were less than one twentieth of the kinetic chain lengths, $\nu = R_p/R_t$. This implies that chain transfer reactions are very important in determining the molecular weights of the polymers. Under these circumstances the polymer size distribution is such that the instantaneous number average molecular weight is half the weight average molecular weight.

The inverse degree of polymerization can be related to the rate of polymerization and to the rate coefficients for the various transfer processes by the equation

$$\bar{P}_n^{-1} = \frac{k_{IM}}{k_p} + \frac{k_{IS}}{k_p} \frac{[S]}{[M]} + \frac{(k_{tc} + 2k_{td})}{k_p^2 [M]^2} \cdot R_p \quad (2)$$

where k_{IM} , k_{IS} are the rate constants for transfer to monomer (M) and polymer (S) respectively. The term, $R_p (k_{tc} + 2k_{td})/k_p^2 [M]^2$ is less than four per cent of the other terms, so that equation (2) can be approximated by

$$\bar{P}_n^{-1} = \frac{k_{IM}}{k_p} + \frac{k_I [S]}{k_p [M]} \quad (3)$$

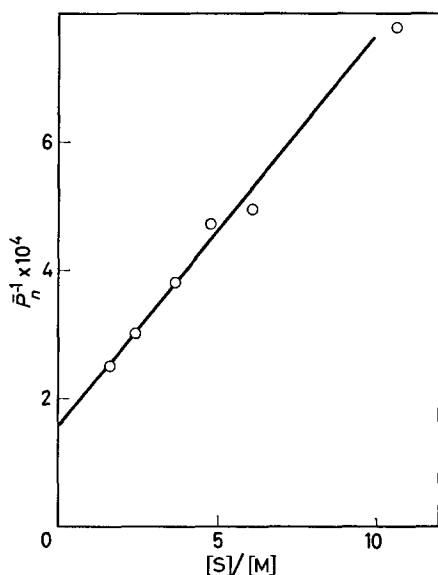


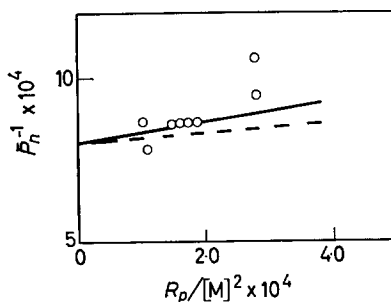
Figure 4—Inverse degree of polymerization against toluene to monomer mole ratio

A plot of the inverse degree of polymerization against the ratio $[S]/[M]$ for polymers prepared at 50°C is illustrated in Figure 4, from which

$$k_{IM}/k_p = 1.5 \times 10^{-4}, \quad k_{IS}/k_p = 0.61 \times 10^{-4}$$

Plots of \bar{P}_n^{-1} against $R_p/[M]^2$ at constant values of $[S]/[M]$ should yield the ratio $(k_{tc} + 2k_{td})/k_p^2$ thus determining whether termination occurs by combination or disproportionation. Such a plot is illustrated in Figure 5, on which are entered the lines for termination by disproportionation and

Figure 5—Inverse degree of polymerization against quotient of rate of polymerization by square of monomer concentration. ○ Experimental points. Full line, calculated assuming termination by disproportionation; broken line, calculated assuming termination by combination



termination by combination calculated from the ratio $(2k_{tc} + 2k_{td})/k_p^2$. While the experimental error does not allow an unambiguous decision to be reached, the results do suggest that disproportionation is the predominant termination process.

The free radical lifetime in a photopolymerization (rate of photopolymerization 3.05×10^{-5} mole litre $^{-1}$ sec $^{-1}$ at 50°C) was found, by the use of intermittent illumination, to be nine seconds.

The value of $(2k_{tc} + 2k_{td})/k_p$ so obtained was 3.1×10^{-4} at 50°C.

Knowledge of all the ratios $(2k_{tc} + 2k_{td})/k_p$, $(2k_{tc} + 2k_{td})/k_p^2$, k_{fM}/k_p , and k_{fS}/k_p allows calculation of the individual rate constants. Values for 50°C are listed in Table 1.

Table 1. Rate constants in the homopolymerization of *N,N*-dimethylacrylamide at 50°C

Rate constant	Magnitude, litre mole $^{-1}$ sec $^{-1}$
k_p	11 000
$2(k_{tc} + k_{td})$	3.8×10^7
k_{fM}	1.65
k_{fS}	0.67

Copolymerization with methylmethacrylate and styrene: copolymer composition

The compositions of a series of copolymers prepared at different monomer feeds were determined by microanalysis, and are illustrated in

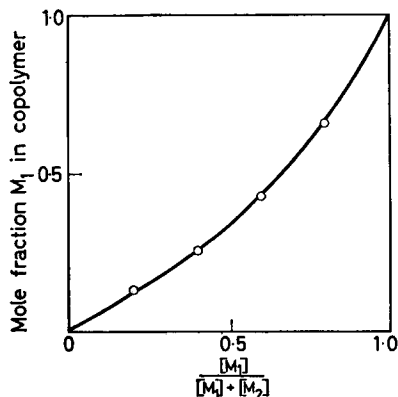
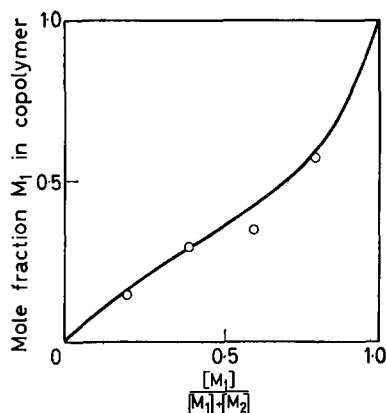


Figure 6—Copolymer compositions, M_1 , *N,N*-dimethylacrylamide, M_2 methylmethacrylate. ○ Experimental points. Line calculated for $r_1 = 0.45$, $r_2 = 1.8$

Figure 7—Copolymer compositions. M_1 , *N,N*-dimethylacrylamide, M_2 , styrene. ○ Experimental points. Line calculated for $r_1=0.23$, $r_2=1.23$



Figures 6 and 7. The reactivity ratios were obtained from the intercepts of plots

$$r_1 = \frac{[B]}{[A]} \left(\frac{d[A]}{d[B]} \right) \left[1 - r_2 \frac{[B]}{[A]} \right] - \frac{[B]}{[A]} \quad (4)$$

and are listed in Table 2.

Also listed in Table 2 are the Alfrey-Price Q , e values for the relevant copolymerizations.

Table 2. Copolymerization parameters at 50°C. M_1 : *N,N*-dimethylacrylamide

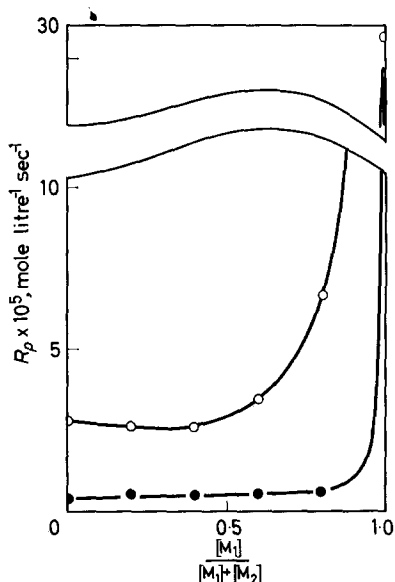
M_2	r_1	r_2	Q_1	Q_2
Methyl-methacrylate	0.45 ± 0.08	1.80 ± 0.18	0.34	0.74
Styrene	0.23 ± 0.13	1.23 ± 0.43	0.33 mean value 0.33	1.0

M_2	e_1	e_2	k_{p12} mole litre ⁻¹ sec ⁻¹	k_{p21} mole litre ⁻¹ sec ⁻¹
Methyl-methacrylate	+0.05	+0.40	24 000	380
Styrene	+0.34 mean value +0.20	-0.8	48 000	110

Copolymerization rates

The rates of copolymerization at 50°C in which the total molarity of both monomers was maintained constant (2.92 mole litre⁻¹ in toluene), and the concentration of initiator was also constant [2.17×10^{-3} mole litre⁻¹] are illustrated in Figure 8. Rates of polymerization were calculated from rates of contraction using the equation of Melville, Noble and Watson⁷.

Figure 8—Copolymerization rate against monomer composition $[M_1] + [M_2] = 2.92$ mole litre⁻¹, $[Init.] = 2.17 \times 10^{-3}$ mole litre⁻¹. ○ M_2 methylmethacrylate; ● M_2 styrene



DISCUSSION

The homopolymerization

The greatest source of error in this work lies in the determination of the rates of initiation. The standard deviation in the measurements was about ten per cent, but considerable doubt is attached to the assumption that each benzoquinone molecule is responsible for stopping one radical chain. Although the assumption seems valid for methylmethacrylate⁸, and in the inhibition of vinyl acetate by duroquinone⁹, it has been reported that benzoquinone may terminate two radical chains in styrene polymerization⁹.

If each benzoquinone molecule is responsible for the termination of two radical chains, the initiator efficiency would be 0.76 and the ratio $k_p/(2k_{tc} + 2k_{td})^{1/2}$ should be 1.25. By comparison with the methacrylate systems, however, and since there is evidence for primary radical recombination in these experiments, the low initiator efficiency seems more reasonable, and we have reported all rate constants on the assumption that one inhibitor molecule terminates one radical chain.

The existence of primary radical termination reactions is inferred from the fact that the monomer kinetic order is 1.4 at high initiator and low monomer concentrations, and that the initiator kinetic order is much less than 0.5 under the same conditions.

A comparison of the propagation rate constant with values for some other common monomers, Table 3, shows that propagation is much more rapid with *N,N*-dimethylacrylamide than for most common monomers, but is less than the unsubstituted acrylamide.

The rate of the propagation reaction is a measure of the reactivity of a radical for its own monomer. However, an assessment of the radical reactivity can be deduced from the velocity of transfer to the same substrate, here toluene.

Table 3. Some propagation rate constants

Monomer	k_p (reference) litre mole ⁻¹ sec ⁻¹	Temperature °C	k_{fs} (reference) litre mole ⁻¹ sec ⁻¹
Styrene	176 ¹⁰	60	0.002 ¹¹
Methylmethacrylate	734 ¹⁰	60	0.015 ¹²
Methylacrylate	2 090 ¹⁰	60	0.564 ¹³
<i>N,N</i> -Dimethylacrylamide	11 000	50	0.67
Acrylamide	18 000 ¹¹	25	—

These constants are also listed in Table 3, and show that the reactivity in this reaction appears to run parallel to the propagation rate constant, but further information on the separate reactivities of monomer and free radical can be more easily deduced from the copolymerization studies.

The copolymerization

It follows from the Q values and the individual rate constants reported in Table 2 that the monomer *N,N*-dimethylacrylamide is less reactive than either styrene or methylmethacrylate, but that the radical is very much more reactive.

The rates of copolymerization are interesting in that when analysed by the conventional rate equation

$$R_p = \frac{R_i^\dagger (r_1 [M_1]^2 + 2 [M_1] [M_2] + r_2 [M_2]^2)}{(r_1^2 \delta_1^2 [M_1]^2 + 2\phi r_1 r_2 \delta_1 \delta_2 [M_1] [M_2] + r_2^2 \delta_2^2 [M_2]^2)^{\frac{1}{2}}} \quad (5)$$

values of the constant ϕ are obtained which are negative and dependent on the monomer feed composition, Table 4. In equation (4), ϕ is defined as

$\frac{k_{t12}}{2(k_{t11}k_{t22})^{\frac{1}{2}}}$: k_{t11} , k_{t22} and k_{t12} represent termination reactions between radicals containing the electrons of unpaired spins on two groups of monomer 1, two groups of monomer 2, and one of each respectively. The constants, δ_1 , δ_2 represent the rate constant ratios $(2k_{t11})^{\frac{1}{2}}/k_{p11}$, $(2k_{t22})^{\frac{1}{2}}/k_{p22}$ respectively.

Table 4. Copolymerization termination parameters

Comonomer	Mole fraction <i>N,N</i> -dimethyl- acrylamide in monomer feed	ϕ	$k_{t(12)} \times 10^{-7}$ litre mole ⁻¹ sec ⁻¹
Methylmethacrylate	1.0	—	3.8
	0.8	-6	0.9
	0.6	-11	1.9
	0.4	-16	2.3
	0.2	-58	1.9
	0.0	—	3.3
Styrene	1.0	—	3.8
	0.8	-2	6.0
	0.6	-62	4.4
	0.4	-120	4.9
	0.2	-320	3.3
	0.0	—	6.5

Quite obviously negative values of ϕ are impossible if such a kinetic equation is correct. It has been suggested^{14,15} that the concept of the ϕ factor in copolymerization requires re-examination when the termination processes are diffusion-controlled. Under these circumstances the relevant rate equation¹⁴ is

$$R_p = \frac{R_i^\dagger (r_1 [M_1]^2 + 2 [M_1] [M_2] + r_2 [M_2]^2)}{k_{t(12)}^\dagger (r_1 [M_1]/k_{p11} + r_2 [M_2]/k_{p22})} \quad (6)$$

where $k_{t(12)}$ is a rate constant which depends not on the end group of the terminating radical, but upon its whole composition. $k_{t(12)}$ thus depends also on the monomer feed composition.

Values of $k_{t(12)}$ calculated using equation (6) are also entered in Table 4, and appear quite reasonable. With methylmethacrylate the rate constant passes through a minimum at intermediate copolymer chain compositions.

In conclusion it may be stated that the free radical polymerization of *N,N*-dimethylacrylamide occurs less rapidly than that of acrylamide, but more rapidly than that of most common monomers. The unusually reactive entity appears to be the free radical rather than the monomer.

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*Department of Inorganic, Physical and Industrial Chemistry,
Donnan Laboratories,
University of Liverpool*

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REFERENCES

- ¹ DAINTON, F. S. and TORDOFF, M. *Trans. Faraday Soc.* 1957, **53**, 499
- ² DAINTON, F. S. and SISLEY, W. D. *Trans. Faraday Soc.* 1963, **59**, 1369, 1377, 1385
- ³ TROSSARELLI, L. and MEIRONE, M. *J. Polym. Sci.* 1962, **57**, 445
- ⁴ SCHULTZ, G. V. *Z. phys. Chem. N.F.*, 1956, **8**, 290
- ⁵ BURNETT, G. M. and COWLEY, P. R. E. *J. Trans. Faraday Soc.* 1953, **49**, 1490
- ⁶ BAWN, C. E. H. and MELLISH, S. F. *Trans. Faraday Soc.* 1951, **47**, 1216
- ⁷ MELVILLE, H. W., NOBLE, B. and WATSON, W. F. *J. Polym. Sci.* 1947, **2**, 229
- ⁸ BEVINGTON, J. C. and GHANEM, R. A. *Trans. Faraday Soc.* 1955, **51**, 946
- ⁹ COHEN, S. G. *J. Amer. chem. Soc.* 1945, **67**, 17; 1947, **69**, 1057
- ¹⁰ MATHESON, M. S., AUER, E. E., BEVILACQUA, E. B. and HART, E. J. *J. Amer. chem. Soc.* 1949, **71**, 497, 2610; 1951, **73**, 1700, 5395
- ¹¹ GREGG, R. A. and MAYO, F. R. *Disc. Faraday Soc.* 1947, **2**, 328
- ¹² BASU, S., SEN, J. N. and PALIT, S. R. *Proc. Roy. Soc. A*, 1952, **214**, 247
- ¹³ DAS, S. K., CHATTERJEE, S. R. and PALIT, S. R. *Proc. Roy. Soc. A*, 1955, **227**, 252
- ¹⁴ ATHERTON, J. N. and NORTH, A. M. *Trans. Faraday Soc.* 1962, **58**, 2049
- ¹⁵ NORTH, A. M. *Polymer, Lond.* 1963, **4**, 134