

STUDIES IN CHAIN-TRANSFER

PART 2.—CATALYZED POLYMERIZATION OF METHYL METHACRYLATE*

BY R. N. CHADHA, J. S. SHUKLA AND G. S. MISRA
Dept. of Chemistry, Lucknow University, Lucknow, India

Received 10th April, 1956

The chain-transfer constants of methyl methacrylate with fourteen solvents, using 2:2'-azobisisobutyronitrile as initiator has been determined at 60° and 80°. The values of chain-transfer as determined at 60° are of the same order as with styrene, showing that the two monomers behave similarly in abstracting an α -hydrogen atom from a solvent. The values of the absolute chain-transfer rates at 60° have been calculated and are found to be approximately half as compared with those of styrene. The energies of activation ($E_{tr, s} - E_p$) and frequency factors [$\ln (A_{tr, s}/A_p)$] for various solvents have also been calculated.

The chain-transfer reaction of methyl methacrylate at 80° C with a variety of solvents in the absence of any catalyst has been studied by Basu, Sen and Palit.¹ These workers² have also made a study of the benzoyl-peroxide-catalyzed polymerization of the same monomer in toluene. In the present paper we report our results on chain-transfer in the 2:2'-azobisisobutyronitrile-initiated polymerization of methyl methacrylate with a variety of solvents at two temperatures.

It has been shown by several workers³⁻⁶ that the aliphatic azonitriles decompose thermally in solution by a true first-order reaction not influenced by solvent or concentration. The studies of Arnett³ on the polymerization of methyl methacrylate in bulk and in benzene solution, using 2:2'-azobisisobutyronitrile as initiator have established that the initial rate of polymerization is proportional to the square root of the initiator concentration and to the first power of monomer concentration. When 2:2'-azobisnitriles are used as initiators in vinyl polymerization, the rate of generation of free-radicals may be set equal to the rate of decomposition of the initiators. Further, the aliphatic nitriles offer a real advantage over benzoyl peroxide in that they are not susceptible to induced decomposition. All these facts make 2:2'-azobisisobutyronitrile an ideal initiator for the purposes of our study.

EXPERIMENTAL

PREPARATION OF MATERIALS

METHYL METHACRYLATE.—Methyl methacrylate was freed from inhibitor by repeatedly washing with potassium hydroxide solution and then with water. After drying over anhydrous magnesium sulphate, it was distilled in vacuum to free it from impurities. It was also carefully fractionated just before use.

SOLVENTS.—The solvents used were the best available reagents (B.D.H. or Eastman Kodak). They were purified by the usual methods, dried and fractionally distilled before use.

2:2-AZOBISISOBUTYRONITRILE.—This compound was prepared in accordance with the method of Overberger *et al.*⁶ It was purified by several recrystallizations from toluene and had a m.p. of 104°. It was stored in a desiccator.

PROCEDURE

Known volumes of methyl methacrylate, solvent and the catalyst were poured into clean glass ampoules. They were thoroughly degassed and sealed under vacuum. These

* The previous publication, "Chain-transfer in the phenylazotriphenylmethane catalyzed polymerization of styrene in toluene" (Chadha and Misra, *Makromol. Chem.*, 1954, 14, 97) is regarded as part 1 of this series.

were then held in thermostats at 60° and 80° C until about 10 % conversion had occurred, as found by visual inspection. The polymers were isolated by precipitation with a large excess of ice-cold methanol and dried to a constant weight.

The specific viscosities were determined in benzene at 25°. The intrinsic viscosities were then obtained by using the expression of Schulz and Blaschke.⁷

$$[\eta] = \frac{\eta_{sp}/c}{1 + k_{\eta} \eta_{sp}} \quad (1)$$

The molecular weights were calculated in accordance with the formula

$$[\eta] = KM^{\alpha}, \quad (2)$$

where $K = 0.57 \times 10^{-4}$ and $\alpha = 0.76$.⁸

THEORETICAL

The general DP equation is

$$\frac{1}{\bar{P}} = C_M + C_S \frac{[S]}{[M]} + C_I \frac{[I]}{[M]} + \frac{\delta^2}{[M]^2} R_p, \quad (3)$$

where C_M , C_S and C_I are the monomer, solvent and catalyst transfer coefficients, R_p is the overall rate of polymerization and δ stands for $k_t^{1/2}/k_p$.

The above equation becomes

$$\frac{1}{\bar{P}} = K(\text{constant}) + C_S \frac{[S]}{[M]} \quad (4)$$

at constant $[I]/[M]$ and if k_t remains constant.

RESULTS

The results of our experiments on the polymerization of different mixtures, e.g., 50 : 50, 40 : 60, 30 : 70, 25 : 75 and 20 : 80 of methyl methacrylate and the various solvents at 60° are presented in table 1. $1/\bar{P}$ has been plotted against $[S]/[M]$ at constant $[I]/[M]$ values. The chain-transfer constants (C_S) are obtained in each case from the slope of these plots and are given in the last column of this table.

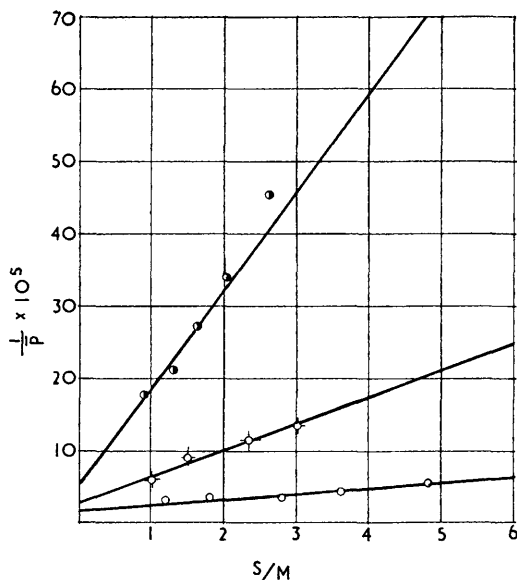


FIG. 1.—Chain-transfer in the catalyzed polymerization of methyl methacrylate with different hydrocarbons at 80° C using 5.0×10^{-3} mole azobisisobutyronitrile per litre monomer.

- , benzene ;
 ⊗, toluene ;
 ●, ethyl benzene

The transfer constants for the same set of solvents as used at 60° have been determined at 80° C and for benzene, toluene and ethyl benzene at 52° C. The plots of $1/\bar{P}$ against $[S]/[M]$ are shown for some of the solvents at 80°, and these are broadly in agreement with the results obtained similarly for the uncatalyzed polymerization of methyl methacrylate by Basu, Sen and Palit.¹

TABLE 1.—TRANSFER CONSTANTS FOR VARIOUS SUBSTANCES WITH METHYL METHACRYLATE AT 60° WITH 50.0×10^{-3} MOLE 2:2'-AZOBISISOBUTYRONITRILE PER LITRE MONOMER

solvent	[S]/[M]	$[\eta]$	$1/\bar{P} \times 10^5$	$1/\bar{P} \times 10^5$ extrap.	$C_s \times 10^5$
benzene	1.204	2.57	7.51		
	1.806	2.32	8.57		
	2.808	2.33	8.52	7.50	0.40
	3.612	2.15	9.53		
	4.817	2.15	9.51		
toluene	1.007	2.45	7.98		
	1.506	2.32	8.65		
	2.347	1.88	11.35	6.80	1.70
	3.018	1.79	12.04		
	4.026	1.63	13.63		
ethyl benzene	0.874	1.47	15.65		
	1.310	1.29	18.66		
	1.622	1.25	19.35	9.00	7.66
	2.038	1.03	24.91		
	2.621	0.99	28.66		
chlorobenzene	1.052	2.29	8.24		
	1.578	2.19	9.26		
	2.455	2.10	9.80	8.25	0.74
	4.210	1.88	11.31		
chloroform	1.341	2.09	9.84		
	2.011	1.60	14.07		
	2.491	1.40	15.63	4.50	4.54
	3.133	1.30	18.47		
carbon tetrachloride	1.109	1.80	12.01		
	2.060	1.20	20.36	2.00	9.25
	3.327	0.84	32.54		
ethylene chloride	1.358	1.82	11.82		
	2.522	1.50	15.22		
	3.169	1.31	18.20	7.00	3.50
	4.074	1.15	21.57		
methylene chloride	1.682	1.85	11.54		
	3.124	1.74	12.57		
	3.925	1.69	13.07	9.50	1.00
	5.046	1.57	14.38		
tetrachloroethane	1.020	1.18	20.92		
	2.380	1.15	21.72		
	3.060	1.08	23.36	18.60	1.55
	4.080	1.03	24.90		
acetone	1.458	1.48	15.50		
	3.402	1.22	20.03	13.50	1.95
	4.374	1.10	22.89		
diethyl ketone	1.013	1.74	12.51		
	1.881	1.33	17.82		
	2.364	1.12	22.50	3.50	8.33
	3.039	0.90	29.68		
<i>isobutyl</i> alcohol	1.042	4.36	3.74		
	1.563	3.94	4.29		
	2.430	3.55	4.91	2.80	1.00
	3.124	2.95	6.28		
<i>t</i> .-butyl alcohol	1.137	4.31	3.80		
	2.237	4.30	3.81		
	2.652	3.81	4.47	2.40	0.85
	3.410	3.23	5.56		
	4.545	2.95	6.29		
<i>isopropyl</i> alcohol	1.114	0.81	34.51		
	2.599	0.72	39.81	27.75	5.83
	3.342	0.63	47.94		
	4.456	0.59	52.65		

DISCUSSION

It is observed that straight lines for $[S]/[M]$ against $1/\bar{P}$ plots for different solvents, on extrapolation, do not meet at one point. This quantity is the value of $1/\bar{P}$ for the bulk polymerization of the monomer at the given $[I]/[M]$ concentration. A similar behaviour has been observed for the uncatalyzed polymerization of methyl methacrylate¹ and the catalyzed polymerization of vinyl acetate.¹² The assumption of active free-radicals formed during transfer reaction as being equivalent to original radicals in propagating chains may not be correct. With certain solvents, the low rate of polymerization by chain-transfer is also possible if the solvent radicals possess sufficient resonance stability. According to Burnett and Melville¹⁹ the reason for the difference in behaviour appears to be that for the short chain compounds the radicals produced by transfer are highly reactive, whereas for aromatics the radicals are relatively inactive so that there is a lag in the propagation of the polymerization chains. Further use of viscosity against molecular weight relationship in calculating the degree of polymerization is not correct, since theoretically only the number average molecular weight has to be used. Most of the low molecular fractions in the polymer are lost during the purification process and an error may be introduced in the calculated molecular weight.

The behaviour of various solvents as chain-transfer reagents are in agreement with the observation of other workers. However, we shall briefly discuss our results in relation to the structure of the various solvents used.

HYDROCARBONS

The chain-transfer constants determined by us for benzene, toluene and ethyl benzene at 80° (fig. 1) are in accord with the data of Basu *et al.*¹ Our results at 60° and 52° C, determined for the first time, also follow the order of reactivity reported by other workers, viz., the availability of α -hydrogen atom attached to the α -carbon atom increases in the order, normal < secondary < primary.

This conclusion is in agreement with the work of Kharasch, McBay and Urry,⁹ who have shown that the radicals from decomposing acetyl peroxide remove the α -hydrogen atoms from ethyl benzene and isopropyl benzene, leaving the substituted benzyl residues to dimerize.

CHLORINATED SOLVENTS

A number of chlorinated solvents have been used with a view to finding their behaviour as chain-transfer reagents. It has been proposed by Mayo¹⁰ earlier that in chlorobenzene chain-transfer takes place through the removal of a hydrogen or chlorine atom. However, from a study of chain-transfer with bromobenzene in the polymerization of styrene, different observations have been made by Mayo.¹⁷ He found that bromobenzene has about the same reactivity as benzene and chlorobenzene in chain-transfer, as measured by the molecular weight of the polystyrene formed. Nevertheless, no significant quantities of bromobenzene were incorporated in the polymer. It is thus concluded that certain aromatic solvents participate in the chain-transfer reaction without permanently combining with the polymer, the net result being the chain-transfer with the monomer.

The chain-transfer with carbon tetrachloride probably takes place through a mechanism already postulated by Price.¹¹ An interesting point to observe is that the value of chain-transfer constants for carbon tetrachloride at 60° and 80° C are about twice those determined for chloroform. This is in contrast with the very high values obtained with carbon tetrachloride and styrene¹³ and also with vinyl acetate, where this value could not be determined as syrupy products were formed.¹²

The chain-transfer constants for methylene chloride, ethylene chloride, tetrachloroethane and chloroform are higher than those of chlorobenzene and may be due to the increased reactivity of the remaining hydrogen atoms caused by halogen substitution.¹³ The chain-transfer with various solvents follows the following order:



It may be remarked that dichloroethane is found to have a higher transfer coefficient than tetrachloroethane. If the chlorine had the effect of increasing the reactivity of the hydrogen, the order of reactivity should have been reversed. It appears probable that here the steric factors come into operation. The availability of hydrogen atoms in tetrachloroethane is hindered due to the large size of the chlorine atoms.

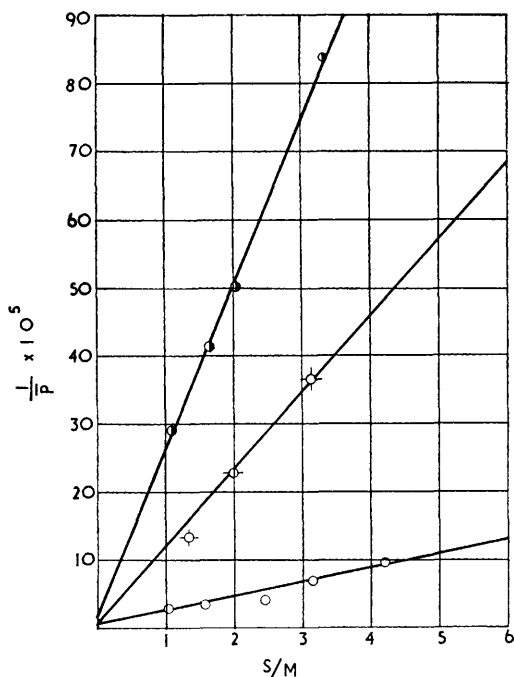


FIG. 2.—Chain-transfer in the catalyzed polymerization of methyl methacrylate with different chlorinated solvents at 80° C using 5.0×10^{-3} mole azobisisobutyronitrile per litre monomer.

○, chlorobenzene; ⊗, chloroform; ●, carbon tetrachloride.

KETONES

Of the two ketones studied, diethyl ketone is found to have a higher transfer coefficient than acetone, as expected. Here an α -hydrogen atom is rendered mobile due to hyperconjugation.

ALCOHOLS

The hydrogen of the hydroxyl group does not seem to take part in the chain-transfer reaction, but only the α -hydrogen atom. In accordance with this hypothesis, it has been found that *isopropyl* alcohol has a higher chain-transfer constant than *t*-butyl alcohol.

DEPENDENCE OF THE CHAIN-TRANSFER CONSTANT ON TEMPERATURE

As is well known, an increase in the temperature of the polymerization always lowers the molecular weight of the polymer, irrespective of whether the chain-transfer or the termination process is the dominant cessation mechanism. Fig. 3 shows the temperature dependence of the chain-transfer in respect of benzene, toluene and ethyl benzene.

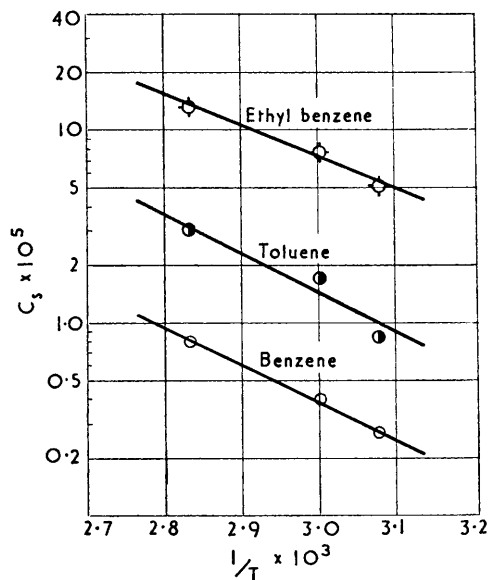


FIG. 3.—Temperature dependence of transfer constants.

From our data on the chain-transfer constants of methyl methacrylate at 60° and 80° C, the temperature independent $E_{tr,s} - E_p$ values and the frequency factors $\ln(A_{tr,s}/A_p)$ by the application of the Arrhenius equation $C = A \exp(-E/RT)$, where $C = k_{tr,s}/k_p$ have been calculated. These values are given in columns 5 and 6 of table 2.

TABLE 2.—TRANSFER CONSTANTS OF VARIOUS SUBSTANCES WITH METHYL METHACRYLATE

solvents	transfer constants $C_S \times 10^5$			$E_{tr,s} - E_p$ (kcal)	$\ln \frac{A_{tr,s}}{A_p}$
	at 60° C	at 80° C	at 52° C		
benzene	0.40	0.80	0.27	8.07	-0.19
toluene	1.70	3.03	0.84	7.76	0.84
ethyl benzene	7.66	13.11	5.01	6.26	0.01
chlorobenzene	0.74	2.07	—	11.98	6.35
carbon tetrachloride	9.25	24.21	—	10.95	7.27
chloroform	4.54	11.29	—	10.59	6.07
ethylene chloride	3.50	7.56	—	8.96	3.33
methylene chloride	1.00	2.17	—	9.02	2.16
tetrachloroethane	1.55	2.35	—	4.85	-3.72
isopropyl alcohol	5.83	19.07	—	13.48	10.70
isobutyl alcohol	1.00	2.29	—	9.61	3.06
<i>t</i> -butyl alcohol	0.85	1.52	—	6.77	-1.42
diethyl ketone	8.33	17.29	—	8.50	3.50
acetone	1.95	2.75	—	4.00	-4.78

COMPARATIVE VALUES OF C_S AND ABSOLUTE VALUES OF TRANSFER RATE

A comparison of the values of chain-transfer constants of some solvents at 60° C in the polymerization of styrene, methyl methacrylate and vinyl acetate is given in table 3. From these the values of the absolute rate of chain-transfer for these monomers has been calculated and is given in the following table.

TABLE 3.—COMPARISON OF CHAIN-TRANSFER COEFFICIENTS AND ABSOLUTE RATE OF CHAIN TRANSFER OF DIFFERENT RADICALS AT 60° C

solvent	$C_S \times 10^5$			$k_{tr, S} \times 10^5$ (mole/l. sec)		
	methyl methacrylate	styrene	vinyl acetate	methyl methacrylate	styrene	vinyl acetate ($10^{-3} k_{tr, S}$)
benzene	0.40	0.18	29.60	146.8	31.7	109.5
toluene	1.70	1.25	208.90	623.8	220.0	772.7
ethyl benzene	7.66	6.70	551.50	2811.0	1180.0	2040.0
chlorobenzene	0.74	—	83.50	271.6	—	308.9
chloroform	4.54	5.00	1251.80	1666.0	880.0	4633.0
carbon tetrachloride	9.25	900.0	—	3384.0	68400.0	—
acetone	1.95	—	117.00	715.7	—	432.9

k_p for methyl methacrylate = 367 at 60° C;^{14a}

k_p for styrene = 176 at 60° C;¹⁵

k_p for vinyl acetate = 3700 at 60° C.^{14b}

According to Nozaki,¹⁶ resonance-stabilized radicals are considered to be less reactive than stabilized ones. α -Methyl containing monomers like methyl methacrylate polymerize to high-molecular-weight polymers with evidence of very low chain transfer with monomer, $C_M = 1.03 \times 10^{-5}$ (Palit *et al.*¹⁸). The polymer radicals from this monomer and styrene are so well stabilized that α -methylene hydrogen abstraction is small or absent. On the other hand, vinyl acetate would be expected to form a very reactive radical. The table shows that chain transfer with solvents for methyl methacrylate is small and of the same order as for styrene. However, the chain transfer with solvents occurs many times faster with vinyl acetate than with methyl methacrylate.

The authors desire to thank Prof. A. C. Chatterji, for facilities and the Scientific Research Grants Committee, U.P., for financial assistance to one of them (R. N. C.).

1 Basu, Sen and Palit, *Proc. Roy. Soc. A*, 1950, **202**, 485.

2 Basu, Sen and Palit, *Proc. Roy. Soc. A*, 1952, **214**, 247.

3 Arnett, *J. Amer. Chem. Soc.*, 1952, **74**, 2027.

4 Lewis and Matheson, *J. Amer. Chem. Soc.*, 1949, **71**, 747.

5 Walling, *J. Amer. Chem. Soc.*, 1949, **71**, 1930.

6 Overberger, O'Shaughnessy and Shalit, *J. Amer. Chem. Soc.*, 1949, **71**, 2661.

7 Schulz and Blaschke, *J. prakt. Chem.*, 1941, **158**, 130.

8 Fox, Conlon, Mason, Schuele and Woodman [from Flory, *Principles of Polymer Chemistry* (Cornell University Press, New York, 1953), p. 312].

9 Kharasch, McBay and Urry, *J. Org. Chem.*, 1945, **10**, 401.

10 Gregg and Mayo, *Faraday Soc. Discussions*, 1947, **2**, 328.

11 Price, *Mechanism of reactions at carbon-carbon double bonds* (Interscience, New York, 1946), p. 61.

12 Palit and Das, *Proc. Roy. Soc. A*, 1954, **226**, 82.

13 Gregg and Mayo, *J. Amer. Chem. Soc.*, 1953, **75**, 3530.

14 (a) Matheson, Auer, Bevilacqua and Hart, *J. Amer. Chem. Soc.*, 1949, **71**, 497.

(b) Matheson, Auer, Bevilacqua and Hart, *J. Amer. Chem. Soc.*, 1949, **71**, 2610.

15 Matheson, Auer, Bevilacqua and Hart, *J. Amer. Chem. Soc.*, 1951, **73**, 1700.

16 Nozaki, *Faraday Soc. Discussions*, 1947, **2**, 337.

17 Mayo, *J. Amer. Chem. Soc.*, 1953, **75**, 6133.

18 Saha, Nandi and Palit, *J. Chem. Soc.*, 1956, 427.

19 Burnett and Melville, *Faraday Soc. Discussions*, 1947, **2**, 322.