

COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B : Chimie

TOME 15 B

ANNEE 1968

Rate of Initiation of Methyl Acrylate Polymerization

by

E. PULAT

4

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

**Communication de la Faculté des Sciences
de l'Université d'Ankara**

Comité de Rédaction de la Série B

S. Saracođlu S. Aybar M. Okay

Secrétaire de Publication

A. Olcay

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifiques représentées à la Faculté : Mathématiques pures et appliquées, Astronomie, Physique et Chimie théoriques, expérimentales et techniques, Géologie, Botanique et Zoologie.

La Revue, à l'exception des tomes I, II, III, comprend trois séries

Série A : Mathématiques, Physique et Astronomie.

Série B : Chimie.

Série C : Sciences naturelles.

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Adrese: Fen Fakóltesi Tebliđler Dergisi, Fen Fakóltesi, Ankara, Turquie.

Rate of Initiation of Methyl Acrylate Polymerization

E. PULAT

*Department of Physical Chemistry, University of Ankara**

(Received 15 January 1968)

Relations between reciprocal number average degree of polymerization and rate of polymerization derived by some workers [1] were applied to the experimental data on the polymerization of methyl acrylate initiated by benzoyl peroxide and azo-bis-isobutyronitrile at 60°C. Chain transfer constants for benzoyl peroxide and azo-bis-isobutyronitrile are zero. Initiator efficiencies of these initiators are close to unity indicating that the termination reaction occurs mainly by disproportionation. The rate expressions of the initiation reaction related to the initiator concentration are given for the two initiators in question.

INTRODUCTION

Tobolsky and Johnson [1] have already shown how the rate of initiation of polymerization is obtained by measuring the number average degree of polymerization. They have studied the bulk polymerization of styrene at 60°C initiated by various initiators.

Tobolsky and Baysal [2] have done a similar and comprehensive study of the bulk polymerization of methyl methacrylate.

In this work we present how our experimental data on the bulk polymerization of methyl acrylate, at 60°C, initiated by benzoyl peroxide and azo-bis-isobutyronitrile fit the kinetic equations given by these workers.

* Mailing address: Ankara Üniversitesi, Fen Fakültesi, Fiziko-Kimya Kürsüsü, Ankara, Turkey.

The relation between reciprocal number average degree of polymerization $1/P_n$, and the rate of polymerization R_p is written [1] as

$$\frac{1}{P_n} = C_m + C_i \frac{[I]}{[M]} + C_s \frac{[S]}{[M]} + AR_p \quad (1)$$

where C_m , C_i , C_s are the chain transfer constant to monomer, initiator and solvent respectively.

$$A \text{ is equal to } (2 k_{td} + K_{tc}) / k_p^2 [M]^2 .$$

when we are dealing with the early stages of polymerization $[M]$ can be taken as the initial monomer concentration, and in this case A is assumed to be constant.

In bulk polymerization the third term on the right hand side of equation (1) is missing. On the other hand, if the chain transfer constant to initiator is neglected, which is reasonable in the range of the initiator concentrations we have used, then equation (1) becomes

$$\frac{1}{P_n} = C_m + AR_p \quad (2)$$

which is called the monoradical line [1].

When the values of $1/P_n$ are plotted against R_p , a curve with the slope of A is obtained.

Since k_p , k_{td} , k_{tc} , which are the specific rate constants for propagation, disappearance of radical pairs by disproportionation and disappearance of radical pairs by combination are all constant at a specified temperature, a constant value should be obtained for A for both initiators used in this work.

Another important behaviour established is that the rate of bulk polymerization is proportional to the square root of initiator concentration:

$$R_p^2 = B [I] \quad (3)$$

where B is a different constant for each initiator and is determined experimentally.

The rate of initiation of monoradical chains evaluated from the steady state condition is as follows

$$R_i = \frac{2 (k_{td} + k_{tc})}{k_p^2 [M]^2} \quad (4)$$

By writing X instead of $k_{td}/(k_{td} + k_{tc})$ which is the fractional part of the termination reaction occurred by disproportionation, and substituting A in equation (4), a modified equation for R_i is obtained.

$$R_i = \frac{2 A}{1 + X} R_p^2 \quad (5)$$

From equation (5) and (3) equation (6) can be written

$$R_i = \frac{2 A B}{1 + X} [I] \quad (6)$$

In this equation A and B are the quantities which can easily be determined; A from the slope of the monoradical line and B , from the square of the slope of the curve R_p versus $[I]^{1/2}$.

Initiator efficiency:

It is generally accepted that some of the radicals produced by decomposition of initiator molecules are not effective in initiating polymeric radical chains.

The effective fraction of the total radicals produced from initiator molecules is given as follows and is called initiator efficiency.

$$f = \frac{R_i}{2 k_d [I]} \quad (7)$$

where k_d is the specific rate constant for the spontaneous decomposition of the initiator.

By substituting equation (6) in equation (7), equation (8) is obtained

$$f (1 + X) = \frac{AB}{k_d} \quad (8)$$

The value of $f(1 + x)$ can be calculated from experimental data, and enables us to decide which type of termination, disproportionation or combination, is predominant by assuming that the value of f is ranging from 50 % to 100 %

EXPERIMENTAL

a) *Purification of Materials:*

Methyl acrylate, benzoyl peroxide, benzene and acetone were purified in the manner described in the previous paper [7].

Azo-bis-isobutyronitrile was recrystallized three times from alcohol-free water then dried in a vacuum dessicator over calcium chloride.

b) *Preparation of Polymethyl Acrylate:*

Polymerization was carried out in the test tubes T shown in Figure 1.

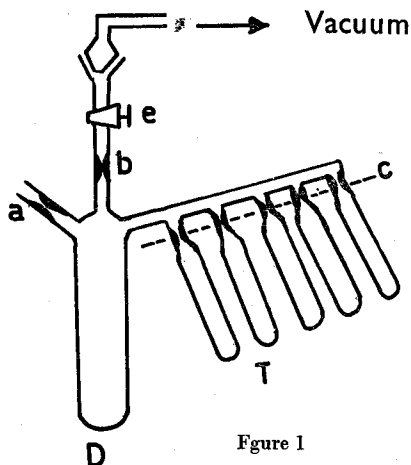


Figure 1

Sufficient amount of initiator solution in chloroform was introduced into D to give the desired initiator concentration in the reaction medium. After evaporating the solvent under high vacuum, freshly distilled monomer was introduced into D. After at least three degassing operations under high vacuum, the apparatus was sealed off from the vacuum line. Each of the test

tubes was filled up with the solution to the labelled level. After sealing off the points C, they were immersed in a thermostat maintained at $60 \pm 0,05^\circ\text{C}$. After the proper reaction time the tubes were removed, cooled with dry-ice methanol mixture and then opened. The tube content was dissolved in acetone. The polymer was precipitated and purified by using cold petroleum ether as precipitant and acetone as solvent, then dried under vacuum, first in cold and then at 40°C to constant weight.

c) *Viscosity Measurements* :

All the viscosity measurements were carried out in the manner explained previously and the relation for calculating the number average degree of polymerization was the same as that used in the previous paper [7].

EXPERIMENTAL RESULTS AND CONCLUSIONS

Figures 2 and 3 show the bulk polymerization of methyl acrylate under different initiator concentrations at 60°C .

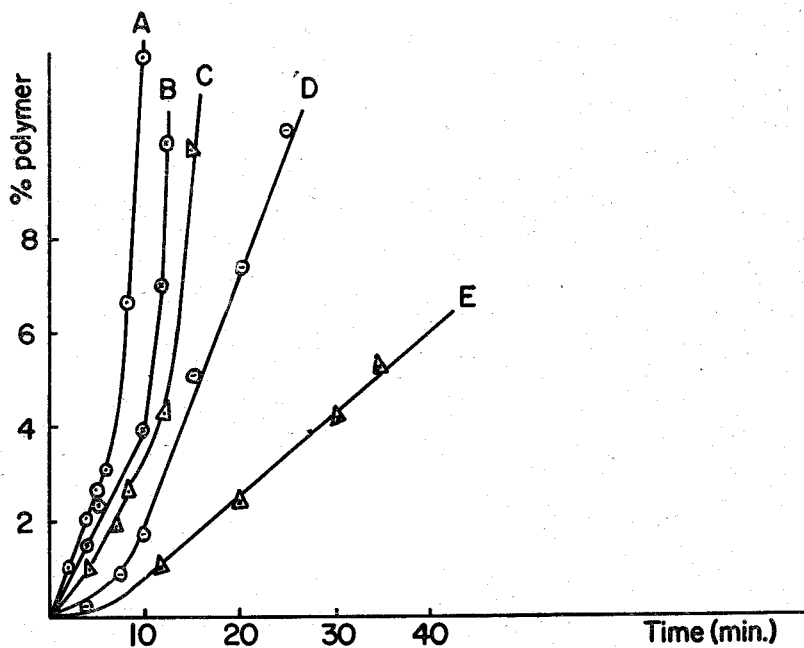


Figure 2. Polymerization of methyl acrylate at 60°C . Curves A, B, C, D, E correspond to the azo-bis-isobutyronitrile concentration of 4.06×10^{-4} , 3.06×10^{-4} , 2.03×10^{-4} , 1.02×10^{-4} , 0.51×10^{-4} mole l^{-1} respectively.

In table I, the rate of the methyl acrylate polymerization and the reciprocal of the number average degree of polymerization of the polymer prepared at different initiator concentrations are tabulated.

The number average degree of polymerization was calculated from viscosity molecular weight relationship given in reference [3]. Intrinsic viscosities of the polymer solutions were determined at 30°C in benzene.

TABLE I

The rate of polymerization and the reciprocal of the number average degree of polymerization of methyl acrylate at 60°C.

Initiator	$[I] \times 10^4$ (mole L ⁻¹)	$R_p \times 10^5$ (mole L ⁻¹ sec ⁻¹)	$(1/P_n) \times 10^5$
AZDN	4.06	99	2.56
	3.06	85	2.44
	2.03	69	2.33
	1.02	49	2.18
	0.51	28	1.99
Bz ₂ O ₂	13.40	118	2.61
	5.36	81	2.38
	2.68	55	2.29
	1.34	42	2.10
	0.67	25	1.95

The curves for the calculated rates of polymerization versus the square roots of the initiator concentrations are shown in Figure 4 for the two initiators.

These experimental curves are in good agreement with equation (3). The values of B we obtained from the squares of the slopes of these straight lines are 2.4×10^{-3} and 1.0×10^{-3} for AZDN and Bz₂O₂ respectively.

Figure 5 shows the plot of $1/P_n$ versus R_p which should be a straight line according to equation (2). Our experimental data fit equation (2) very well for both initiators. This indicates that the chain transfer constants C_1 for these two initiators are negligible. From the slope and intercept of this line we have calculated the values of A and C_m to be 7×10^{-3} and 1.8×10^{-3} respectively.

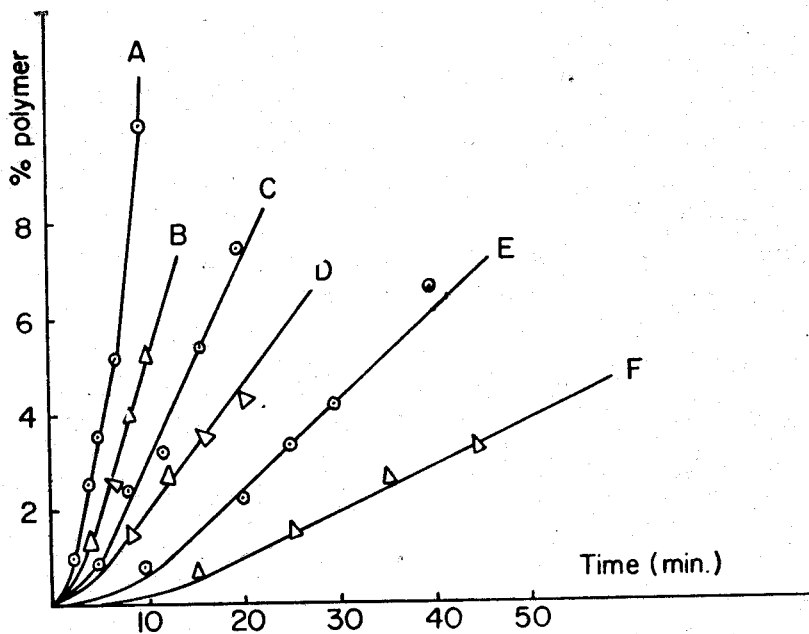


Figure 3. Polymerization of methyl acrylate at 60°C. Curves A, B, C, D, E, F correspond to the benzoyl peroxide concentration of 13.4×10^{-4} , 5.36×10^{-4} , 2.68×10^{-4} , 1.34×10^{-4} , 0.67×10^{-4} , 0.34×10^{-4} mole l^{-1} respectively.

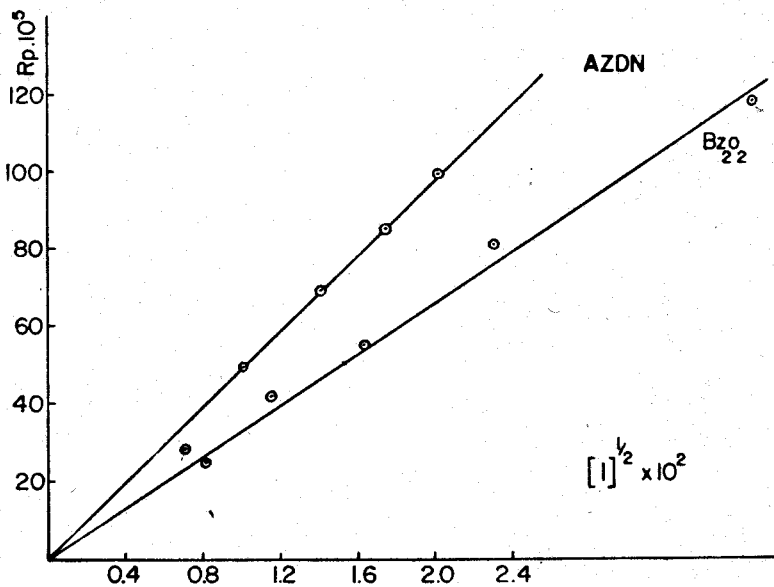


Figure 4. Rate of polymerization versus the square root of the initiator concentration.

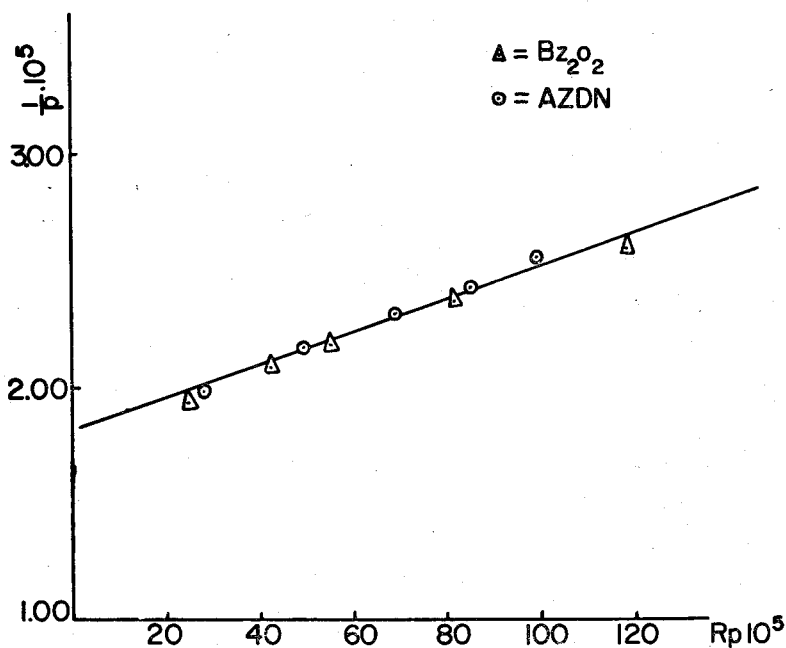


Figure 5. Rate of polymerization versus reciprocal number average degree of polymerization of methyl acrylate.

For comparative purposes, the kinetic constants of the bulk polymerization of some monomers at 60° C are tabulated in Table II.

TABLE II

Monomer	Initiator	A	B	C_m	C_I
Methyl methacrylate [2]	Bz_2O_2	8.28	4×10^{-7}	1×10^{-5}	0
	AZDN		8.59×10^{-5}		0
Styrene [1]	Bz_2O_2	12.3	1.21×10^{-7}	6×10^{-7}	0.048
	AZDN		5.19×10^{-7}		0
Methyl acrylate [a]	Bz_2O_2	7×10^{-3}	1.0×10^{-3}	1.8×10^{-3}	0
	AZDN		2.4×10^{-3}		0

[a] in this study

By using the experimental values of A and B, the rate expression of the initiation reaction of the methyl acrylate polymeri-

zation is given for both initiators in Table III with the values of two other monomers

TABLE III

Comparison of the rates of initiation of styrene, methyl methacrylate and methyl acrylate polymerizations initiated by AZDN and Bz_2O_2

Styrene [1]	Methyl methacrylate [2]	Methyl acrylate [a]
$R_i = \frac{1.28 \times 10^{-5}}{1 + X} [AZDN]$	$R_i = \frac{1.42 \times 10^{-5}}{1 + X} [AZDN]$	$R_i = \frac{3.36 \times 10^{-5}}{1 + X} [AZDN]$
$R_i = \frac{2.96 \times 10^{-6}}{1 + X} [Bz_2O_2]$	$R_i = \frac{6.62 \times 10^{-6}}{1 + X} [Bz_2O_2]$	$R_i = \frac{14 \times 10^{-6}}{1 + X} [Bz_2O_2]$

[a] in this study

INITIATOR EFFICIENCY

According to the definition of the initiator efficiency we use the following equations

$$f = R_i / 2 k_d [I]$$

$$f(1 + X) = AB/k_d$$

By substituting our experimental values for A and B, and the values of k_d given in references [4], [5] for AZDN and Bz_2O_2 we have calculated the values of $f(1 + X)$ for the methyl acrylate polymerization.

The values of $f(1 + X)$ and the initiator efficiencies for three monomers are tabulated in Table IV.

TABLE IV.

The values of $f(1 + X)$ and the initiator efficiencies for three monomers.

Monomer	$f(1 + X)$	Initiator	f
Styrene	0.66	Bz_2O_2	0.66
	0.70	AZDN	0.70
Methyl methacrylate	0.91	Bz_2O_2	0.91
	0.77	AZDN	0.77
Methyl acrylate	1.83	AZDN	0.92
	1.89	Bz_2O_2	0.95

If termination reactions in the styrene and methyl methacrylate polymerizations occurred by combination of radical pairs then x would be zero, as the result of this the initiator efficiency would range from 66 to 91 % as shown in Table IV.

Whereas for methyl acrylate if X was zero, then the initiator efficiencies for both initiators would range from 1.83 to 1.89 % which is never possible. If all terminations occurred by disproportionation then x would be unity and the initiator efficiencies would range around 90 % which is the most acceptable case [8].

Thus we think that our experimental data in Table IV for methyl acrylate speak in favor of termination by disproportionation.

There is some evidence to support this conclusion. The recent studies on different plastics have shown that when the polymers degrade on exposure to high energy radiations, termination reaction occurs primarily by disproportionation. Some of our polymers have been irradiated by gamma rays [6] and it was found that our polymers show a great tendency towards degradation.

ÖZET

Bazı araştırmacılar [1] tarafından verilen sayıca ortalama polimerizasyon derecesinin tersi ile polimerizasyon hızı arasındaki bağıntı, etil akrilatın benzoil peroksit ve azo-bis-izobütironitril ile 60°C da başlatılan polimerizasyonunda elde edilen deneysel neticelere uygulandı.

Benzoil peroksit ve azo-bis-izobütironitril için zincir transfer sabitleri sıfırdır. Bu başlatıcıların polimerizasyonu başlatma tesirliliği bire yakın olup; bu durum, sonlanma reaksiyonunun başlıca disproporsiyonasyonla olduğuna işaret eder. Bu çalışmada polimerizasyonun başlama reaksiyonu hız ifadesi, başlatıcı konsantrasyonuna bağlı olarak, adı geçen her iki başlatıcı için verilmektedir.

ACKNOWLEDGEMENT

I wish to thank Dr. C. Şenvar for clarifying many aspects of the subject and for continued advice and encouragement.

REFERENCES

- [1] A. V. Tobolsky and D. H. Johnson, J. Am. Chem. Soc., 74, 938 (1952)
- [1] A. V. Tobolsky and B. Baysal, J. Polymer Sci., 8, 529 (1952)
- [3] S. D. Gadkary and S. L. Kapur, Makromolekülare Chem., 17, 29 (1955)
- [4] P. D. Bartlett and K. Nozaki, J. Am. Chem. Soc., 68, 2377 (1946)
- [5] M. S. Matheson and F. M. Lewis, J. Am. Chem. Soc., 71, 747 (1949)
- [6] C. B. Şenvar and A. Tuğsavul, Commun., Fac., Sci., Univ., Ankara 12 B, 21 (1965)
- [7] C. B. Şenvar and E. Pulat, Commun, Fac. Sci. Univ., Ankara, 15 B, 25 (1968)
- [8] M. S. Matheson, E. E. Auer, E. B. Bevilacqua, E. J. Hart, J. Am. Chem. Soc., 73, 5395 (1951)

Prix de l'abonnement annuel 1967:

Turquie : 15 TL ; Etranger : 30 TL.

Prix de ce numéro : 5 TL (pour la vente en Turquie).

**Prière de s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı
Ankara Turquie.**