COMMUNICATIONS

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

Série B : Chimie

TOME 15 B ANNEE 1968

The Solution Polymerization of Methyl Acrylate and Determination of The Chain Transfer Constant for Acetone

by

E. PULAT and C. B. ŞENVAR

3

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

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

La Revue "Communications de la Faculté des Sciences de "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 etre accompagnés d'un bref sommaire en langue turque.

Adrese: Fen Fakültesi Tebliğler Dergisi, Fen Fakültesi, Ankara, Turquie.

The Solution Polymerization of Methyl Acrylate and Determination of The Chain Transfer Constant for Acetone

E. PULAT** and C. B. ŞENVAR*

Department of Physical Chemistry, University of Ankara, Turkey.–

(Received 15 january 1968)

The initiated polymerization of methyl acrylate is studied in the presence of carbon tetrachloride, chloroform, acetone and petroleum ether at 60°C.

Benzoyl peroxide was used as the initiator. The transfer constant for acetone has been found to be 2.3×10^{-5} at 60° C.

Using the transfer constant value found by Gadkary and Kapur [3] at 80°C for the same solvent, we have also calculated the value of $E_{tr\text{-}S} - E_p$ and $\log (A_{tr\text{-}S}/A_p)$.

By measuring the rate of polymerization of methyl acrylate in bulk, at three different temperatures, the apparent activation energy of polymerization has been determined. From this we have calculated the activation energy of the termination reaction, since the activation energy E_d, for the decomposition of the initiator, and E_p, for the propagation reaction are konown.

INTRODUCTION

In vinyl polymerization reactions, the presence of some solvents causes a considerable decrease in the molecular weight of polymer molecules.

It was first pointed out by Flory [6] that in the presence of certain solvents a side reaction called "chain transfer reaction" is taking place.

It has been generally established that chain transfer takes place by the loss of hydrogen atoms in hydrocarbon solvents whereas

---

* present address: Hacettepe Universitesi, Ankara-Turkey.

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

in chlorinated solvents such as carbon tetra chloride, these reactions are brought about by the transfer of chlorine atoms.

The stationary radical concentration is unaffected by the chain transfer reaction and hence the polymerization rate is unaltered assuming that the new active centres produced by transfer processes are as reactive in chain propagating as the original radicals.

Besides bimolecular termination one alternative way of producing polymer molecules is the chain transfer reaction. Consequently more polymer molecules are produced per unit time. Since the rate of monomer disappearance is unaltered, the number average degree of polymerization is decreased. Consequently the average degree of polymerization of the polymer obtained in the presence of any transfer agent will be lower then that in the absence.

Transfer reactions are especially important in controlling the average molecular weights of commercially produced polymers.

Much work has been done in this field and there has still been a growing interest in the chain transfer behaviour of many solvents.

The following well known equation is used to calculate the chain transfer effect of any solvent.

$$\frac{1}{P} = \frac{1}{P_0} + K_c \frac{[S]_0}{[M]_0}$$

where P and P_0 are the number average degree of polymerization with and without solvent respectively, K_c is the chain transfer constant, representing the ratio of the rate constants for chain transfer and chain growth.

A plot of $1/P$ against $[S]_0/[M]_0$ is clearly linear with a slope numerically equal to the transfer constant K_c, so it is sufficient to measure the number average degree of polymerization of the polymers prepared in a mixture at different $[S]_0/[M]_0$ ratios. The subscript "o" is used to indicate the original concentrations of solvent and monomer.

EXIPERIMENTAL

a) *Purification of Materials*

1– Methyl Acrylate: 1.5 liters of monomer was washed with two 250-ml portions of 2 % ferrous sulfate solutions. It was then washed twice with water followed by two washings with 250 - ml portions of 2 % solution of sodium hydroxide in water. The monomer was again washed with water and was then dried over anhydrous sodium sulfate. It was distilled at a boiling point at 116 mm. Hg and was stored under nitrogen in a dark and cold place [1].

2 . *Benzoyl Peroxide:* It was recrystalyzed three times from chloroform and the product was dried in a vacuum dessicator for three days before using [2].

3 . *Acetone, Carbon tetrachloride and chloroform:* They were distilled under atmospheric pressure. The boiling points of the collected liquids were 53-54 °C, 73 °C, 58 °C respectively.

4 . *Petroleum ether:* The fraction collected at 60–80 °C was redistilled and the fraction boiling at 63–65 °C was used in our work.

b) *Preparation of Polymers*

Procedure: Polymerization was carried out in Pyrex test tubes; the diameter and the lenght of the tubes were 1″ and 6″ respectively.

The apparatus used in our axperiments is shown in Figure 1.

Before starting the experiment, the apparatus was thoroughly cleaned and dried. A known amount of benzoyl peroxide was dissolved in chloroform. 5 ml from this solution was introduced into D, then the apparatus was connected to the vacuumline to evaporate the chloroform. After evaporation of the solvent, a certain amount of methyl acrylate and the transfer agent were introduced into D. This mixture was degassed, at least three times under 10^{-4} — 10^{-5} mm Hg After sealing off the apparatus from the line, the solution was poured from D into the test tubes T. Then each of them was sealed off at the point C by cooling with dry ice – methanol mixture. The tubes were then suspended in a thermostat at 60° ± 0.05 °C, and polymerization was carried out to about 5 % conversion. After the proper reaction time, the tubes were then removed, cooled and opened. The polymer was precipitated by using cold petroleum ether as precipitant and acetone as solvent. Polymethyl acrylate so abtained was dried in vacuum for several days.

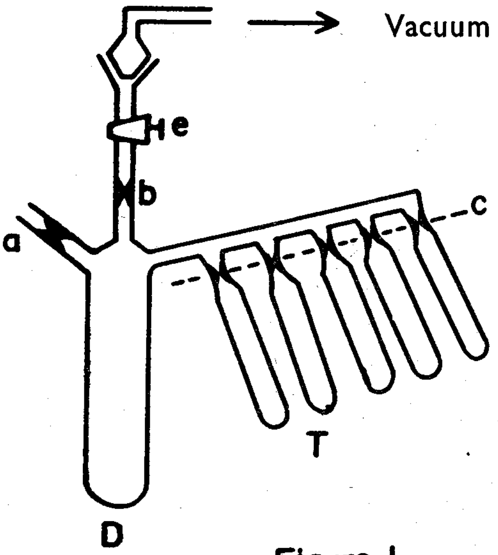

Figure. I

c) *Viscosity Measurements*

Intrinsic viscosities of the polymers were obtained by measuring the viscosities of polymer solutions in benzene at 30 °C, with an Ostwald viscometer having a flowtime of 106 seconds for the solvent. The concentrations of the solutions were always less than 0 .250 g per 100 cc. of solvent.

The number average degree of polymerization was calculated from the following equation

$$[\eta] = KM^{\alpha}$$

The values of the constants K and a were taken from the literature [3] as $K = 1.28 \times 10^{-4}$ and $a = 0.7143$.

Experimental Results and Conclusion.

The variation of per cent polymerization with time is shown in Figure 2 for the polymerization of methyle acrylate in three different solutions. Solvent concentration was 40 % by volume and initiator concentration was 5.36×10^{-3} mole L^{-1}

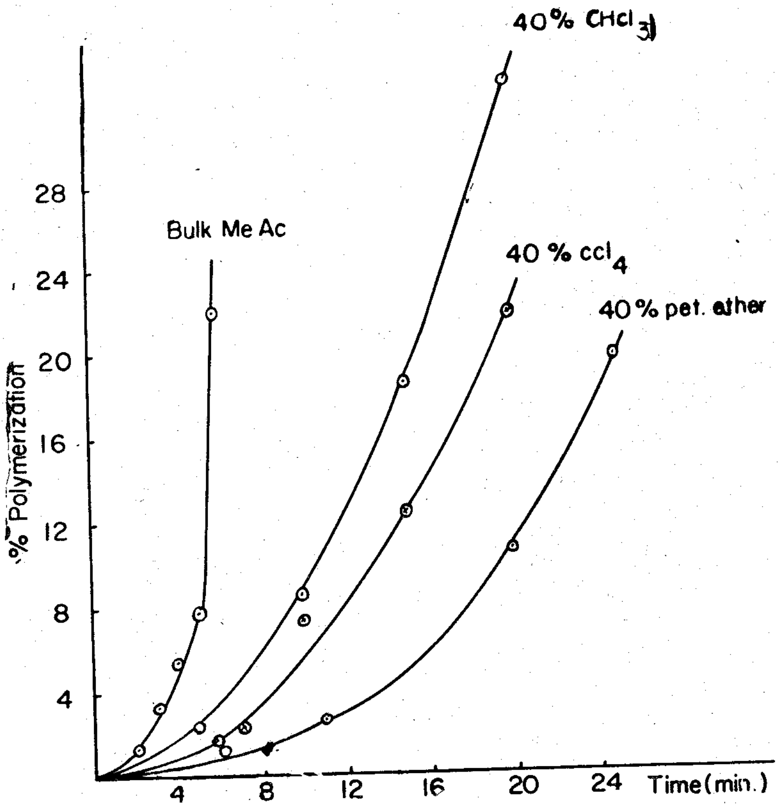

Figure 2. Solution polymerization of methyl acrylate at 60 °C, $[Bz_2O_2] = 5.36 \times 10^{-3}$ mole l^{-1}

Figure 3 illustrates the effect of the solvent and precipitant on the rate of polymerization.

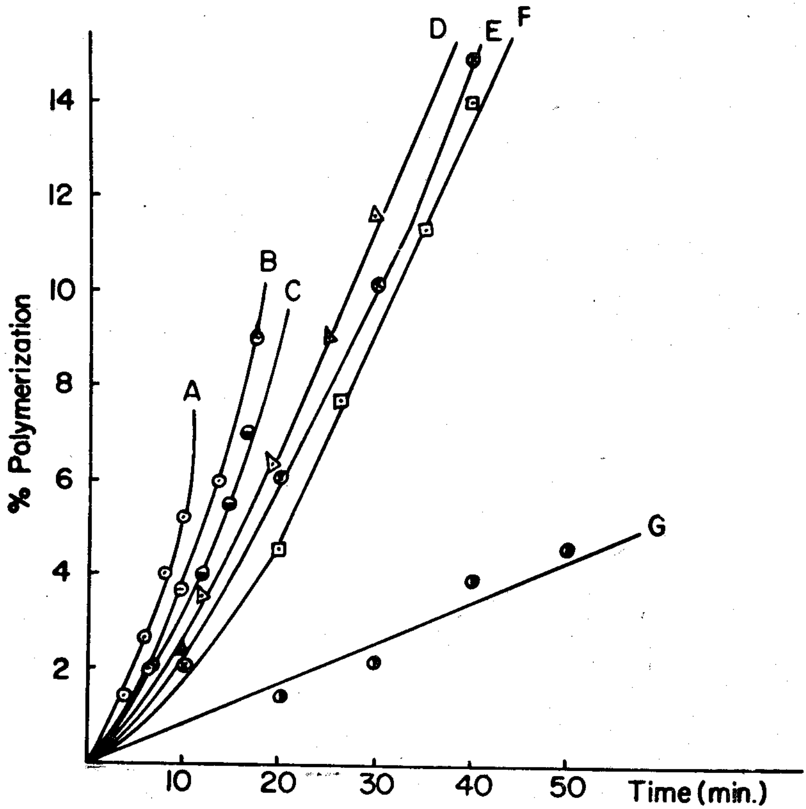

Figure 3. Curve A corresponds to the bulk polymerization of methyl acrylate, curves B, D, F correspond to 15, 30, 40 per cent acetone by volume respectively; curves C, E, G correspond to 15, 30, 40 per cent petroleum ether by volume respectively.

Except curve G, the reaction medium was homogeneous and viscous during the polymerization. In the case of G, the mixture was heterogeneous, The rate of the polymerization of methylacrylate in the prerence of 40 % acetone was distinctly higher than that in the presence of petroleum ether.

This result is in good agreement with the fact that the rate of termination is lower in the viscous medium than in the non-viscous medium.

Norrish and Smith [10] attributed this decrease in k_t to the high viscosity of the medium. They also demonstrated that the moleculer weight of the polymer produced in the viscous medium is higher. This has been justified by measuring the molecular weight of the polymers prepared in the presence of different amount of acetone and petroleum ether. Our experimental results are shown in Figures 4 and 6.

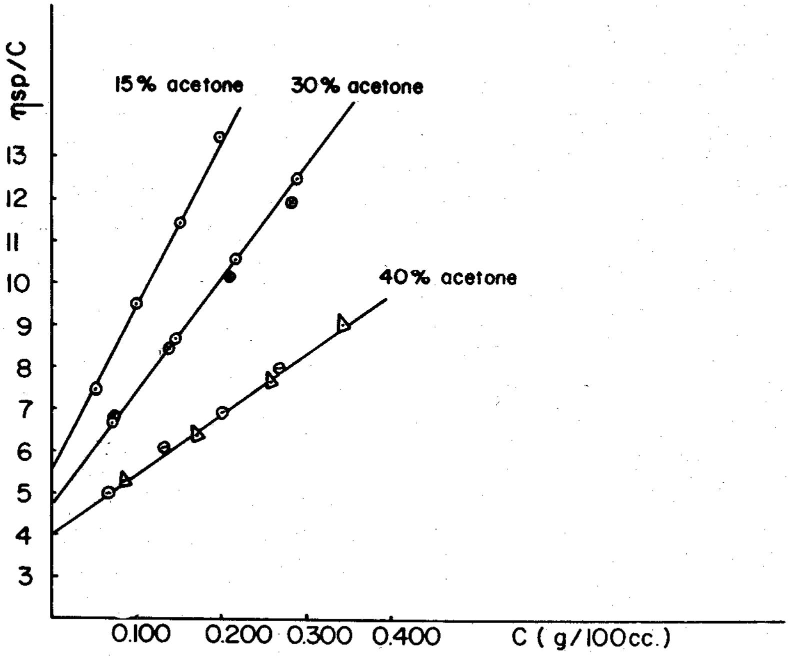

Figure 4. The plot of ηsp /C versus C for polymethyl acrylate prepared in the medium having three different acetone concentrations. ⊙, 2.19 % pol.; ⊙, 3.61 % pol.; ⊙, 4.55 % pol.; △, 4.23 % pol.

From Figures 4 and 6 one can also see another theoretically expected result:That the number average degree of polymerization decreases as the original monomer concentration is lowered.

The intrinsic viscosity values and the calculated number average degrees of polymerization of the polymers produced in the mixture having various amount of acetone as solvent are tabulated in Table I.

TABLE I

The intrinsic viscosities and the reciprocal of the number average degree af polymerization of the polymers produced in the mixture having various amount af acetone

Acetone (volume %)	$[\eta]$	$(1/p) \times 10^5$	[S] / [M] (x 10)
15	5.5	2.83	2.17
30	4.7	3.52	5.28
40	4.0	4.41	8.20

The curve based on the third and forth columns is shown in Figure 5.

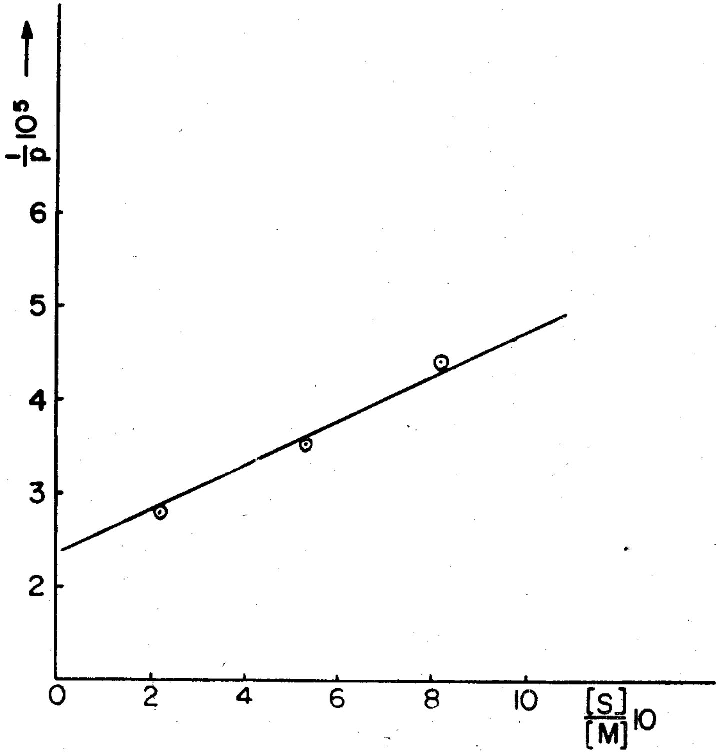

Figure 5. Reciprocal number average degree of polymerization versus [S] / [M]

Transfer constant for acetone found from the slope of this line is 2.3 x 10^{-5}.

The value of K_c obtained by us for acetone and those reported elsewhere for the same solvent but different monomers are compared in Table II.

TABLE II

Chain Transfer Constants for Acetone

Monomer	Initiator	Temperature	K_c x 10^5
Methyl acrylate	Bz_2 O_2	80 °C	11(3)
Methyl acrylate	Bz_2 O_2	60 °C	2.3 our result
Me. methacrylate	Uncatalyzed	80 °C	2 .25(4)
Vinyl acetate	Bz_2 O_2	75 °C	42(4)
Styrene	Bz_2 O_2	80 °C	41(5)

Comparison of our K_c value with that given in reference [3] clearly shows that the transfer constant increases as the temperature is increased.

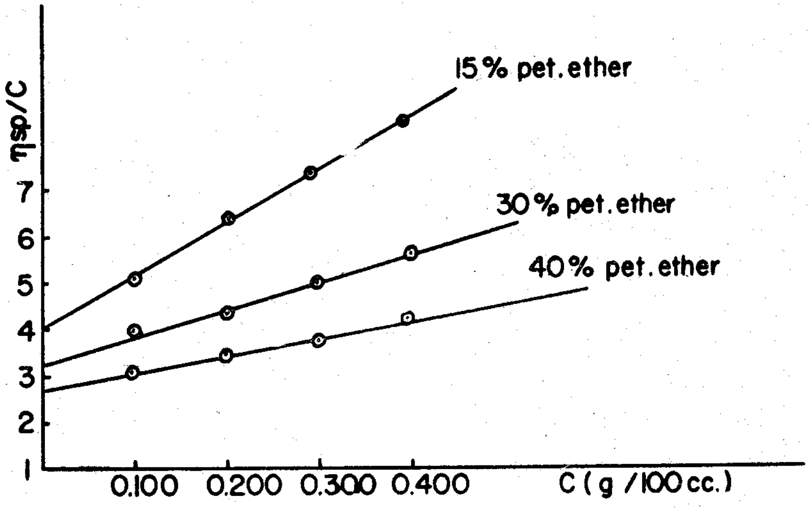

Figure 6. The plot of ηsp /C versus C for polymethyl acrylate prepared in the medium having three different petroleum ether concentrations.

This means that transfer reaction is affected by the change of temperature more than the rate of propagation reaction is. This is in good egreement with the fact that the activation energy of transfer reaction is higher than that of the propagation reaction.

By using Kapur's and our K_c values found at two different temperatures (80 and 60 °C) $E_{tr-S} - E_p$ and log (A_{tr-S}/A_p) have been calculated.

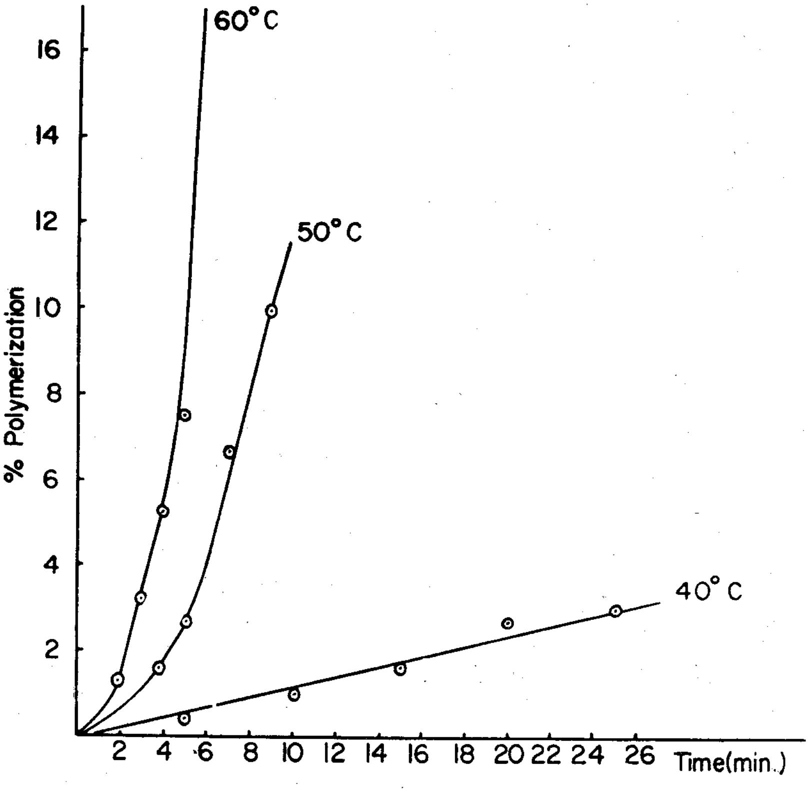

Figure 7. Polymerization of methyl acrylate at three different temperatures, $[Bz_2O_2] = 5.36 \times 10^{-3}$ mole l^{-1}

Taking 7 .1 kcal and 1×10^3 from reference [7] for the value of E_p and A_p, we have calculated the values of E_{tr-S} and A_{tr-S} to be 25 .4 k cal and 2×10^{15} respectively.

Comparison of the rate constants of the transfer and propagation reactions obtained at two different temperatures shows that low transfer constants go hand in hand with high activation energy E_{tr-S}.

The frequency factor for transfer exceeds that for propagation; hence the higher activation energy for chain transfer is responsible for the lower rate of transfer reaction.

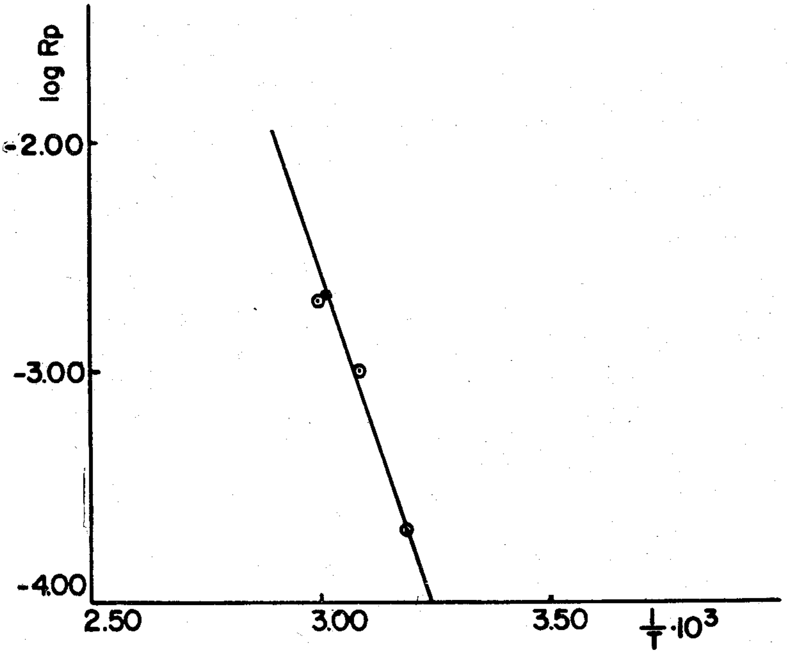

Figure 8. Plot of Log Rp versus 1/T

The activation energy for transfer generally exceeds that for propagation by 15 k cal; so our value seems to be a bit high which may be due to taking the K_c values of two different workers.

All the values on which our calculations are based and the results are tabulated in Table III.

TABLE III.

The frequency factors, activation energies and rate constants for the transfer and propagation reaction of methyl acrylate

Temperature (°C)	K_c ($x10^5$)	K_p (l $mole^{-1}$ sec^{-1})	$K_{tr\text{-}s}$ (l $mole^{-1}$ sec^{-1})	E_p (Kcal-$mole^{-1}$)	$E_{tr\text{-}s}$ (Kcal-$mole^{-1}$)	A_p (l $mole^{-1}$ sec^{-1})	$A_{tr\text{-}s}$ (l $mole^{-1}$ sec^{-1})
60	2.3(a)	2090(7)	0.048(a)	7.1(7)	25.4(a)	$1x10^8$ (7)	$2x10^{15}$(a)
80	11(3)	3840(a)	0.423(a)				

(a) our experimental and calculated results using the data taken from reference [7]

As the last part of this study we present the apparent activation energy of the methyl acrylate polymerization.

For this purpose we have polymerized methyl acrylate in the bulk state using benzoyl peroxide as the initiator. The concentration of the initiator was 5.36×10^{-3} mole l^{-1}.

This part of our study is shown in Figures 7 and 8. The apparent activation energy E_a is 26.9 k cal. The activation energy of the termination reaction E_t was calculated to be 9.6 k cal by taking 7.1 and 30 kcal [11] for the values of E_p and E_d respectively, and using the following relationship

$$E_a = E_d / 2 + (E_p - E_t/2)$$

ÖZET

60°C da başlatıcı olarak benzoil peroksid kullanılarak, aseton, petrol eteri ve karbon tetraklorür yanında metil akrilatın polimerizasyonu incelendi. Bu sıcaklıkta aseton için transfer sabiti 2,3 x 10^{-5} olarak bulundu.

80°C da Gadkary ve Kapur [3] tarafından aynı çözücü için bulunan transfer sabitinden faydalanılarak $E_{tr\text{-}s} - E_p$ ile log $(A_{tr\text{-}s}/A_p)$ in değeri de hesaplandı.

Çözücü ihtiva etmeyen bir ortamda, üç ayrı sıcaklıkta metil akrilatın polimerizasyon hızı ölçülerek reaksiyonun ektivasyon enerjisi tayin edildi. Başlatıcının parçalanma reaksiyonu aktivasyon enerjisi E_d ile polimerizasyonun sürdürme kademesi aktivasyon enerjisi E_p bilindiğinden sonlanma reaksiyonu aktivasyon enerjisi E_t hesaplandı.

REFERENCES

[1] J. L. Kice, J. Polymer Sci., 19, 123 (1965)

[2] A. V. Tobolsky and B. Baysal, J. Polymer Sci., 8, 529 (1952)

[3] S. D. Gadkary and S. L. Kapur, Macromoleculare Chem., 17, 29 (1955)

[4] S. L. Kapur and R. M. joshi, j. Polymer Sci. 14, 489 (1954)

[5] S. L. Kapur, J. Polymer Sci. 11, 399 (1953)

[6] P. J. Plory, J. Am. Chem. Soc., 59, 241 (1937)

[7] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, J. Am. Chem. Soc., 73, 5395 (1951)

[8] M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, J. Am. Chem. Soc., 73, 1700 (1951)

[9] M. S. Matheson, E. E. Auer, E. B. Bevilacque and E. J. Hart, J. Am. Chem. Soc., 71, 2610 (1949)

[10] R. G. W. Norrish and R. R. Smith Nature, 150, 336 (1942)

[11] P. J. Flory, Principles of Polymer Chemistry (Cornell University press İTHACA, New York 1953), Chap. 4, p. 124

Prix de l'abonnement annul 1967:

Turquie : 15 TL ; Etranger : 30 TL.
Prix de ce numéro : 5 TL (paurla vente en Turquie).
Prière be s'adresser pour l'abonnement à : Fen Fakültesi Dekanlığı
Ankara Turquie.

Ankara Üniversitesi Basımevi - 1968