COMMUNICATIONS

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

Série B: Chimie

TOME 23 B ANNÉE 1974

Determination of k_p^2/k_t in the Polymerization of Methyl Acrylate and the Equation of Rate of Termination

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

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Adresse: Fen Fakültesi Tebliğler Dergisi, Fen Fakültesi‘ Ankara, Turquie.

Determination of k_p^2/k_t in the Polymerization of Methyl Acrylate and the Equation of Rate of Termination

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(Received 24.X.1974)

SUMMARY

The values of k^2_p/k_t for methyl acrylate polymerization initiated by benzoyl peroxide and azo-bis izobutyronitrile have been determined. By using Matheson's values for k_p and k_t, k^2_p/k_t has been calculated. From these results, it is seen that the equation of rate of termination must be given without the factor 2 which is used by some polymer chemists.

INTRODUCTION

Rate of polymerization of vinyl monomers for the free radical polimerization is given as follows when percentage conversion of monomer to polymer is low.

$$R_p = k_p \left(\frac{2k_i}{k_t}\right)^{1/2} [I]_o^{1/2} \cdot [M]_o \qquad (1)$$

In this equation it is assumed that all the primary radicals produced from the decomposition of initiator molecules are capable of starting polymerization reaction.

From the avobe equation we can write the equation (2)

$$\frac{k^2_p}{k_t} = \frac{R^2_p}{2k_i\,[I]_o \cdot [M]_o} \qquad (2)$$

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In the equation (2), $[I]_o$ and $[M]_o$ are the initiator and monomer concentration inially taken. Therefore their numerical values are known. Rate of polymerization, R_p, can be determined experimentally. k_i is the rate constat for the decomposition of the initiator used, so from the equation (2) the experimental value of k^2_p/k_t can be calculated.

EXPERİMENTAL

In this experiment benzoyl peroxide and azo–bis–izobutyronitrile are used as initiator. Purification of these materials and monomer was given in reference [1].

Polymerization reaction was carried out in the pure monomer at 60°C. Percent polymerization was not higher then two. All the experimental results are shown in Table I and Table II.

TABLE I

$[M]_o$ = 10,45 mole l^{-1}; $k_i = 1{,}2 \times 10^{-5}$ sec^{-1}; Initiator: AZDN

R_p (mole l^{-1} sec^{-1})	$[I]_o$ (mole l^{-1})	k^2_p/k_t (1 $mole^{-1}$ sec^{-1})
3.8×10^{-4}	0.5×10^{-4}	11×10^{-1}
7.0×10^{-4}	2.0×10^{-4}	9.3×10^{-1}
8.5×10^{-4}	3.0×10^{-4}	9.2×10^{-1}
9.9×10^{-4}	4.0×10^{-4}	9.3×10^{-1}

TABLE II

$[M]_o$ = 10.45 mole l^{-1}, $k_i = 3.7 \times 10^{-6}$ sec^{-1}, Initiator: Bz_2O_2

R_p mole l^{-1} sec^{-1}	[I] mole l^{-1}	k^2_p/k_t (1 $mole^{-1}$ sec^{-1})
2.4×10^{-4}	0.5×10^{-4}	14×10^{-1}
4.4×10^{-4}	1.8×10^{-4}	13×10^{-1}
5.5×10^{-4}	2.7×10^{-4}	14×10^{-1}
8.1×10^{-4}	5.4×10^{-4}	15×10^{-1}
11.8×10^{-4}	13.4×10^{-4}	13×10^{-1}

Using the values of k_p and k_t, which are given for the same monomer in reference [2], k^2_p/k_t has been calculated as 9.2×10^{-1} and 9.5×10^{-1}.

It is obvious from the above results that in the free radical

polymerization of the vinyl monomers the rate of termination will be given [3,4]

by

$$R_t = k_t [C^{\cdot}]^2_s$$

but not by

$$R_t = 2k_t [C^{\cdot}]^2_s$$

which is used by some polymer chemists [5].

ÖZET

Benzoil peroksit ve azo bis izo bütironitril kullanılarak metil akrilatın polimerizasyonuna ait k^2_p/k_t değerleri denel olarak tayin edilmiştir. Öte yandan aynı sıcaklıkta bu monomere ait Metheson'un verdiği k_p ve k_t değerlerinden de k^2_p/k_t hesaplanmıştır. Elde edillen sonuçlardan sonlanma hız ifadesinde bazı polimer kimyacıların kullandığı 2 faktörünün bulunmaması gerektiği kanısına varılmıştır.

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Prix de l'abonnement annuel

Turquie : 15 TL; Étranger: 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.

Ankara Üniversitesi Basımevi, Ankara – 1975