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A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISAANCE

Solution Polymerization of Ethyl Acrylate in Benzene, Acetone and Cyclohexane

by

E. PULAT And M. TALU

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Faculté des Sciences de l'Université d'Ankara
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DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

Solution Polymerization of Ethyl Acrylate in Benzene, Acetone and Cyclohexane

E.PULAT and M.TALU

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SUMMARY

In this study the effect of solvent on the transfer reaction of the solution polymerization of ethyl acrylate was investigated. For these reactions three different solvents benzene, acetone and cyclohexane were chosen. At 60°C temperature, the transfer constant of these solvents were found as $3.75x10^{-5}$ for benzene; $4.52x^{-5}$ for acetone and $4.40x10^{-5}$ for cyclohexane. From these values it was seen that benzene had the lover transfer effect than acetone and cyclohexane.

INTRODUCTION

Some workers [1] have been previously studied on the solution polymerization of ethyl acrylate in acetone and cyclohexane. At 80 °C temperature, the value of the transfer constant of acetone was biger than the other solvents. In this work we have studied at 60 °C temperature.

Transfer constants K_s of these solvents were found by using Mayo aquation,

$$\frac{1}{\bar{DP}} = \frac{1}{\bar{DP}_o} + K_s \frac{[S]_o}{[M]_o}$$

EXPERIMENTAL

a) Purification of Materials: Ethyl acrylate was purified by the method given in reference [2]. Benzoyl peroxide used as initiator was purified by recrystalizing three times from chloroform as described previously [3]. Acetone, benzene and cyclohexane were purified by vacuum distillation; acetone, benzene and cyclohexane were collected at 53–54 °C; 76–76,5 °C and 76 °C respectively. n-Hexane which was used as precipitant was also purified by distillation. The fraction boiling at 63.5–65 °C was collected.

b) Preparation of Polymers: All the polymerization reactions were carried out in the sealed pyrex tube under high vacuum. Before use all the glassware were dried. Benzoyl peroxide was dissolved in the purified chloroform. Its concentrations were determined. 5 ml of benzoyl peroxide solution was poured in the reaction tube. The solvent was pumped off to leave the solid benzoyl peroxide, then the required volume of monomer and solvent were transferred to the reaction tube by using a pipette. The reaction mixture was degassed at least three times under high vacuum, then the reaction vessel sealed off from the vacuum line and was put in a thermostate for limited time.

Polyethyl acrylate was precipitated from the diluted reaction mixture by usig n-hexane and dried in vacuum oven at 40 ° C.

c) Rate of Polymerization: Rates of polymerization of these reactions were found by usig gravimetric method. The dried polymer samples were carefully weighed. Rate of polymerization was calculated by using the folloving equation

$$R_p = \frac{\text{Pol}\ \% \times [\,M]_o}{6 \times 10^3 \times t} \quad (\text{mol.l}^{-1}.\text{sec}^{-1})$$

d) Molecular Weight Measurement: Viscosity-average molecular weights $\bar{M}_v$, were measured by using Ubbelohde viscometer with the use of benzene as solvent. From the intrinsic viscosity velues, the molecular weights of polyyethyl acrylate samples were calculated by using the following relation reported in reference[4].

$$[\eta] = 27.7 \times 10^{-5}\ \bar{M}_v^{0.67}$$

All the experimental results are given in Tables I and II. From the data given in Table I, $1 / \overline{DP}$ and $[S]_o / [M]_o$ values were calculated. The Figures I, II, III were obtained by plotting $1 / \overline{DP}$ versus $[S]_o / [M]_o$. From the slopes of these Figures the transfer constants of these solvents were calculated as 4.52×10^{-5} for acetone; 3.75×10^{-5} for benzene; 4.40×10^{-5} for cyclohexane.

Table I

Solvent	Solv. (vol%)	[η] (dl/g)	$\bar{M}_v$
Acetone	15	5.076	2,306,000
	30	4.359	1,837,000
	40	3.477	1,311,000
	60	2.489	795,900
Benzene	15	6.060	3,002,000
	30	5.200	2,380,000
	50	3.660	1,403,000
	70	2.410	758,400
Cyclohexane	15	2.730	913,500
	30	2.570	834,000
	40	2.350	730,500
	60	2.102	618,400

Table II

Solvent	Solv.(vol.%)	Time(min.)	Polymer(g)	Pol %	$R_p x10^3$
Acetone	15	10	2.9622	15.119	1.972
	30	15	1.2707	7.875	0.564
	40	19	1.4736	10.655	0.516
	60	30	2.2300	24.186	0.495
Benzene	15	6	1.8492	9.438	2.050
	30	15	2.7860	17.266	1.236
	50	10	0.6316	5.480	0.421
	70	15	0.8094	11.704	0.359
Cyclohexane	15	11	6.1010	31.139	3.693
	30	12	2.5818	16.001	1.433
	40	12	1.6137	11.668	0.895
	60	18	15.482	16.792	0.572

All the results are tabulated in Table III.

By comparing our results with the other's we come to this conclusion that in the polymerization of ethyl acrylate, acetone is more effective transfer agents than the two solvents under these circumstances.

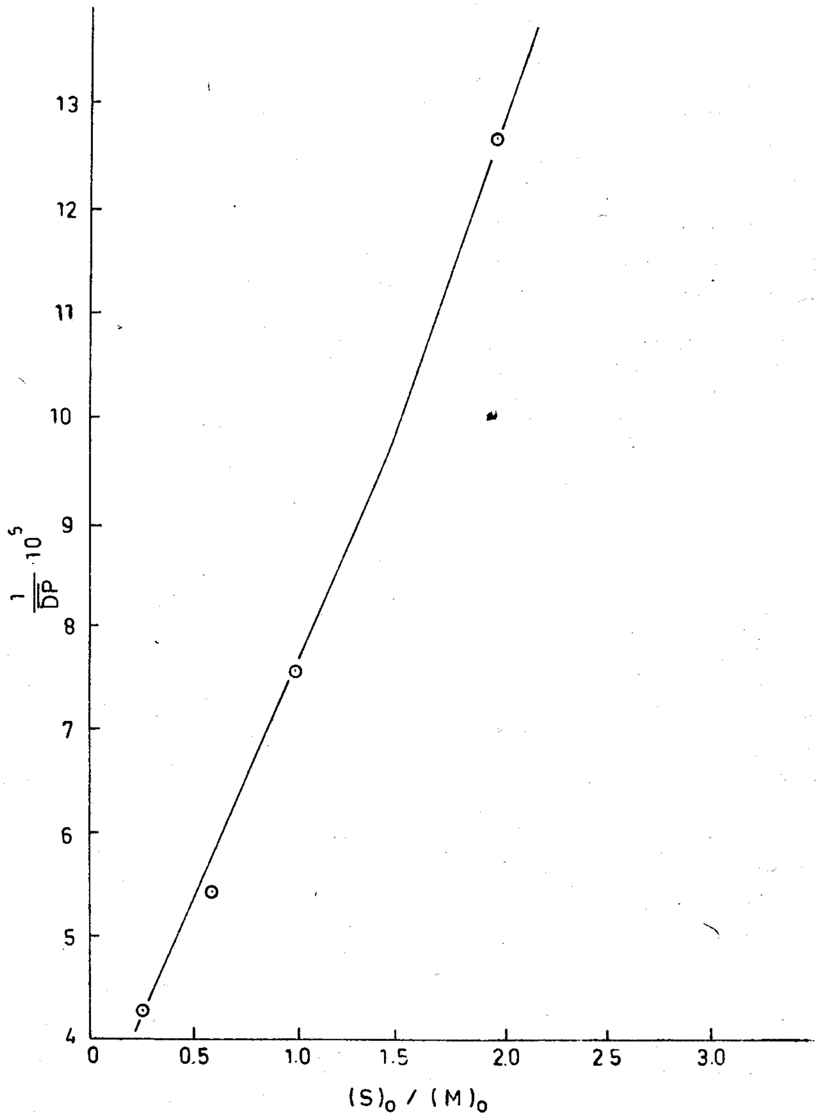

FIGURE I $1/\overline{DP}$ V.S $(S)_o / (M)_o$ FOR POLETHYL ACRYLATE PREPARED IN ACETONE AT 60°C

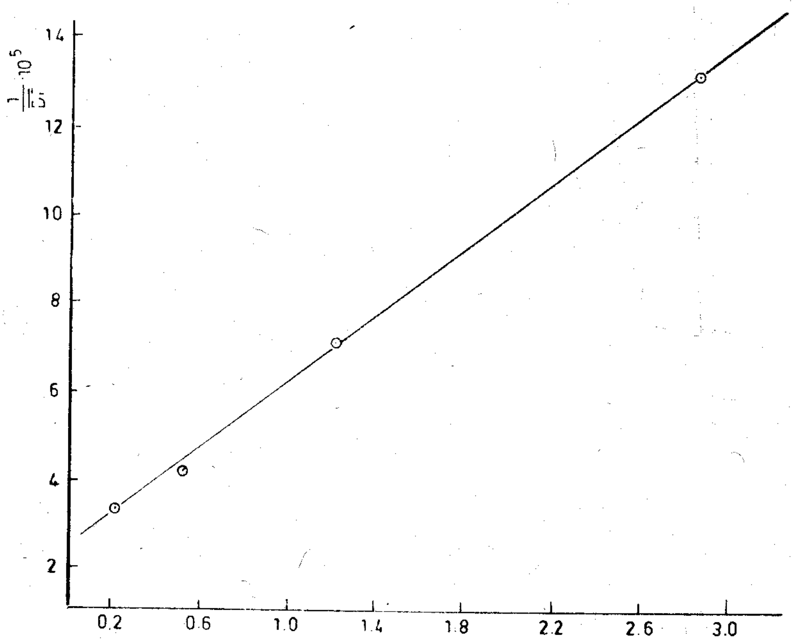

FIGURE II $1/\overline{DP}$ V.S $(S)_0/(M)_0$ FOR POLYETHYL ACRYLATE PREPARED IN BENZENE AT 60°C

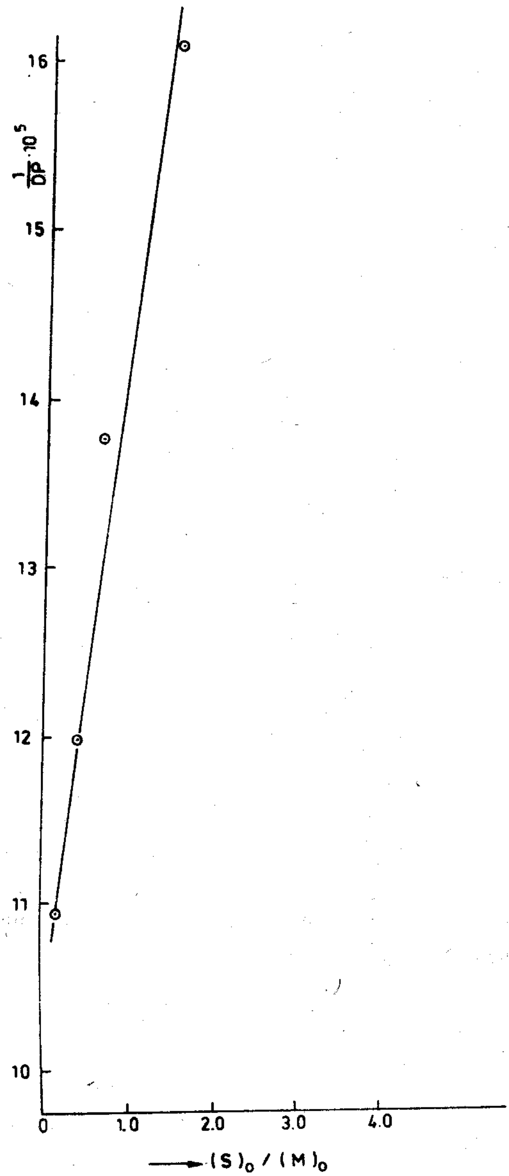

FIGURE: III $\frac{1}{\overline{DP}}$ V.S $\frac{(S)_o}{(M)_o}$ FOR POLYETHYL ACRYLATE PREPARED IN CYCLOHEXANE AT 60°C

Table. III

Solvents	Solv. (vol. %)	$1/\bar{DP}x10^5$	$[S]_o/[M]_o x10$	$K_s x10^5$
Acetone	15	4.342	2.607	
	30	5.450	6.330	
	40	7.637	9.848	
	60	12.580	22.165	4.52
Benzene	15	3.335	2.154	
	30	4.206	5.231	
	50	7.136	12.206	
	70	13.208	28.482	3.75
Cyclohexane	15	10.960	1.772	
	30	11.994	4.302	
	40	13.707	6.693	
	60	16.190	15.064	4.40

ÖZET

Bu çalışmada üç ayrı çözücüde etil akrilatın çözelti polimerizasyonu yapılmıştır. Benzen, aseton ve siklohegzanın çözücü olarak kullanıldığı çalışmada adı geçen çözücülere transfer sabitleri sırasıyla 3.75×10^{-5}; 4.52×10^{-5}; 4.40×10^{-5} olarak bulunmuştur. Transfer sabitlerinin değerinden de anlaşılacağı gibi polietil aktilat radikali benzenle transfere ötekilerden daha az yatkındır. Bunun uzun ve kısa zincirler elde etmek bakımından teknik bir önemi vardır.

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