Volume : 2 | Issue : 5 | May 2013 • ISSN No 2277 - 8160

Research Paper

Science

Kinetic Studies On The Radical Polymerization On N-Octyl/Dodecyl Itaconates

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ABSTRACT

The bulk copolymerisation of di-n-octyl/dodecyl itaconate (OI/DDI) and styrene initiated with AIBN was kinetically investigated. The polymerisation rate (Rp) was expressed by: Rp = k[AIBN]0.5. The polymerisation of di-n-octyl itaconates/dodecyl itaconates showed an activation energy of 18.23 kcal/mol (POI)/ 17.64 kcal/mol in the temperature range of 60-90oC.It was obsereved that rate of polymerisation increased with an increase in temperature/ or initiator concentration. In order to investigate the effect of time, copolymerisation of di-n-octyl/dodecyl itaconates and styrene was carried out for 20, 25, 30 & 35 minutes. When Rp was plotted against time (t) a straight line was obtained indicating that the rate of polymerisation varies linearly with time. The effect of initiator concentration and reaction time an intrinsic viscosity, molecular weight and molecular weight distribution was also investigated. Thermal stability of the samples was determined using the thermogravimetric analysis.

KEYWORDS:

Introduction:

The radical polymerization of vinyl monomers is known to be more sensitive to the steric effect due to the substituents of monomers compared to ionic polymerisations. For examples, α-methylstyrene shows no homopolymerizability in usual radical polymerisation, while it is easily polymerised by cationic initiators. Recently, however, some fumarate esters, a,b-di-substituted ethylene, were found to homopolymerize at relatively high rates to high polymers, where the bulkiness of ester alkyl group accelerates the polymerisation [1-3]. It is also of interest that itaconate esters polymerise at moderate rates to yield their polymers of high molecular weights despite two bulky substituents of the monomer [4-5]. Considerable attention has been paid to the solution properties of itaconate polymers [6-8]. The present paper describes the results of kinetics studies on the radical polymerisation of n-octyl/n-dodecyl itaconate and styrene initiated with AIBN azo initiator.

EXPERIMENTAL

Materials

Itaconic acid (Aldrich), 1-octanol (CDH), 1-dodecanol (CDH), sodium bicarbonate (SRL), aluminium oxide (CDH), methanol (SRL) and toluene (Qualikems) were used as supplied.

Styrene was purified by washing with 10% sodium hydroxide and then with water followed by distillation under reduced pressure. Azobisisobutyronitrile (AIBN) (High Polymer Labs) was recrystallised from chloroform. Tetrahydrofuran (Qualikems) was dried by passing sodium wire followed by distillation. Di-n-octyl(OI)/di-n-dodecyl itaconates(DI) monomers were synthesized by reacting one mole of itaconic acid with 2 moles of n-octanol/n-dodecanol using toluene as the solvent and p-toluene sulphonic acid as the catalyst.

PROCEDURE

The detailed procedure for the synthesis and characterization of di-alkyl itaconates is reported in our previous paper. [9]. In order to determine the rate of copolymerisation, the reaction was carried out in nitrogen atmosphere for different intervals of time i.e. 20, 25, 30, 35 min. using 0.1% (w/w) AIBN as an initiator at 60±1°C. Equimolar ratio of the monomers i.e. OI : styrene/DI : styrene were taken in the initial feed in a three necked flask equipped with nitrogen inlet tube and condenser. After passing N_2 for 10 min., 0.1% (w/w) AIBN was added to the continuously stirred reaction mixture. After desired intervals of time, the contents of the flask were poured with continuous stirring in to excess of methanol. The precipitated copolymers were filtered using the preweighed G-3 sintered glass crucible and dried in vacuum oven at 50-60°C till constant weight and then re-weighed to evaluate the percentage conversion. The effect of temperature on the copolymerisation of OI/DI with styrene (0.5:0.5) was investigated at different temperatures i.e. 50, 60, 70, 80°C and the rate of copolymerisation at different temperatures was determined as described above.

The copolymerisations were also carried out at 60°C in nitrogen atmosphere using different initiator concentrations i.e. 0.5, 0.1, 0.125, 0.15, 0.175, 0.2% (w/w) for studying the effect of initiator concentration on the rate of copolymerisation. Copolymers have been designated by adding a prefix P to the monomer designation of n-alkyl itaconate followed by a numerical suffix indicating the amount of initiator. For example a copolymer prepared by taking 1%, 1.25% of AIBN have been designated as POI-100, POI-125 and PDDI-100 , PDDI-125. With effect of temperature copolymer have been designated by POI-100(40), POI-100(50) means copolymer prepared at 40°C and 50°C respectively.

RESULTS AND DISCUSSION

Table 1. Effect of initiator concentration on rate of polymerisation Time= 35 min, Temp= 60° C

Sample Designation	AIBN(%) (w/w)	% conversion	Rate of polymerisation conversion/min %
POI-100	1.00	3.0	0.08
POI-125	1.25	5.6	0.15
POI-150	1.50	8.72	0.23
POI-175	1.75	11.4	0.30
POI-200	2.00	16.4	0.44
PDDI-100	1.00	10.0	0.28
PDDI-125	1.25	12.8	0.36
PDDI-150	1.50	14.4	0.41
PDDI-175	1.75	17.03	0.48
PDDI-200	0.20	19.03	0.54

Table 2. Effect of temperature on rate of polymerisation Time=35 min, AIBN= 1%

Sample Designation	Temp(°C)	% conversion	Rate of polymerisation conversion/min %
POI-100(40)	40	1.4	0.03
POI-100(50)	50	2.0	0.05
POI-100(60)	60	5.6	0.15
POI-100(70)	70	25.6	0.63
POI-100(80)	80	35.2	0.95
PDDI-100(60)	60	10.0	0.28
PDDI-100(70)	70	26.2	0.74
PDDI-100(80)	80	29.6	0.84

Table 3. Effect of time on rate of polymerisation Temp=60°C, AIBN= 1%

Sample Designation	Reaction time min	% conversion	Rate of conversion/min
POI	25	4.1	0.16
POI	30	4.8	0.16
POI	35	5.6	0.16
POI	40	7.2	0.18

The copolymer of OI/DI with styrene (0.5: 0.5 molar ratio) was investigated kinetically in bulk. From fig 4 showed the slope of the plot of % conversion Vs time, R_p was calculated and was found to be increased with increasing initiator and temperature respectively.

Fig. 1 Plot of variation of rate of polymerisation vs. square root of initiator concentration for n-octyl itaconate : styrene.

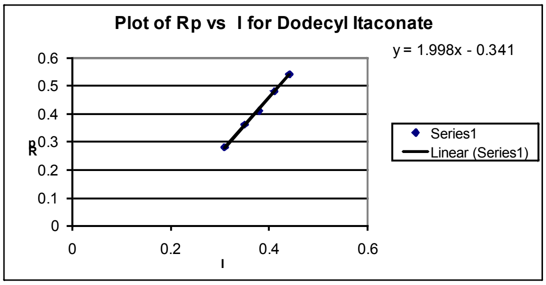


Fig.2 Plot of variation of rate of polymerisation vs. square root of initiator concentration for n-dodecyl itaconate : styrene.

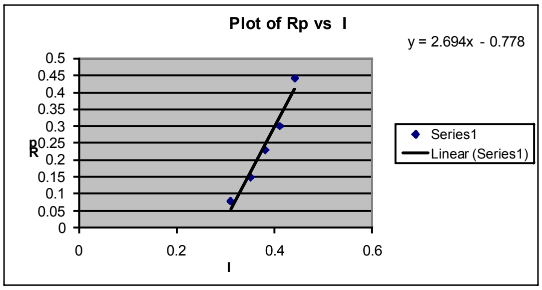


Fig.3 Arhenius plot for n-octyl itaconate : styrene copolymer system

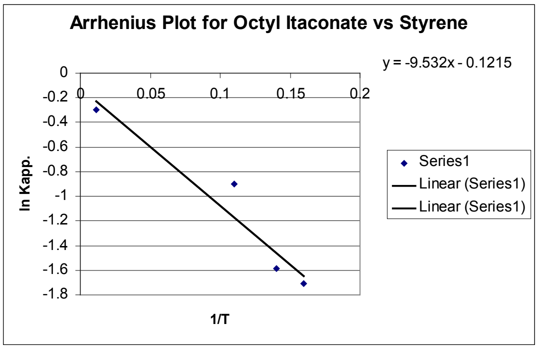
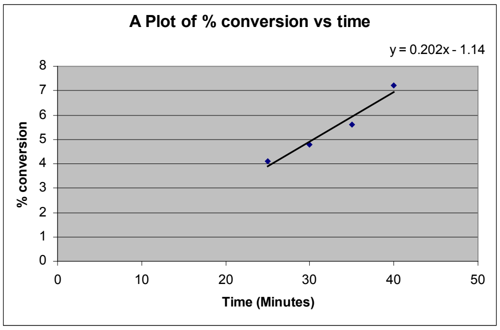


Fig.4 A plot of % conversion Vs time



Effect of initiator concentration

The effect of initiator concentration on rate of copolymerisation of equimolar amounts of n-octyl/n-do-decyl itaconates and styrene was studied. It was observed that rate increased with an increase in the initiator concentration (Table 1). Plots of Rp vs $I^{1/2}$ are shown in Fig. 1. and Fig. 2. A linear relationship was observed indicating thereby that the rate of copolymerisation was dependent on the half power of the initiator concentration. This implies that the termination was either by combination or disproportionation. No departure from polymerisation kinetics explain the absence of side reactions especially primary radical termination

Effect of temperature

In order to investigate the effect of temperature, copolymerisation of equimolar amounts of n-octyl/n-do-decyl itaconates and styrene was carried out at 50, 60, 70, 80°C. Overall rate constant (K_{app}) was determined by plotting the primary experimental data, reaction time (t) and monomer conversion (x) at different temperatures according to the following equation.[10]

$$-\ln(1-x) = K_{app}[I_0]^{0.5}t$$

The overall rate constant can be related to overall activation energy by the Arrhenius equation.

$$K_{app} = A e^{-E_0/RT}$$

$$\ln K_{app} = \ln A - E_0/RT$$

where E_0 = overall activation energy
A = frequency factor

When ln K_{app} was plotted against 1/T, a straight line was obtained (Fig. 3) whose slope was equal to the activation energy. The activation energy in the temperature range of 60-80°C was found to be 18.23 Kcal./mol (POI) and 17.64 Kcal/mol. For PDDI copolymer this value is slightly lowest as compared to AIBN initiated polymerisation of styrene or methyl methacrylates[11] but slightly higher than reported for the homopolymerisation of n-butyl itaconate monomer using AIBN as initiator[12].

Intrinsic viscosity of n-octyl/n-do-decyl itaconates and styrene copolymers was determined in THF at 30±1°C. The value of [h] in copolymers decreased with increasing initiator concentration or temperature. The results of intrinsic viscosity are summarized in Table 3.

The M_n, M_w and molecular weight distribution of copolymers were calculated by GPC using polystyrene (having molecular weight 5,40,000, 1,56,000, 47,500, 22,000 and 1700) as calibration standards. As expected, molecular weight (M_n, or M_w) decreased with increasing initiator concentration/or temperature. The results are summarized in Table 4. All the samples had polydispersity index in the range of 1.46-1.89.

Table 4a. Effect of initiator on the intrinsic viscosity, molecular weights and polydispersity index of homopolymers and copolymers

Sample Designation	[η]ml/g	M_w´10^3	M_n´10^3	PDI
POI-100	21.0	68	37	1.82
POI-125	16.0	63	33	1.89
POI-150	14.5	42	24	1.72
POI-175	9.0	38	22	1.68
POI-200	6.0	28	16	1.66
PDDI-100	15.0	72	46	1.55
PDDI-125	12.0	60	39	1.52
PDDI-150	10.0	59	39	1.50
PDDI-175	8.0	46	32	1.46
PDDI-200	6.0	41	22	1.89

Table 4b. Effect of temperature on the intrinsic viscosity, molecular weights and polydispersity index of and copolymers

Sample Designation	[h]ml/g	M_w´10^3	M_n´10^3	PDI
POI-100(50)	18.0	106	65	1.64
POI-100(60)	16.0	63	33	1.89
POI-100(70)	12.0	26	16	1.57

POI-100(80)	9.0	20	11	1.70
PDDI-100(60)	15.0	72	46	1.55
PDDI- 100(70)	13.0	24	14	1.70
PDDI-100(80)	9.0	14	9	1.54
PDDI-100(90)	6.0	8	6	1.35

Table 5. Results of Thermogravimetric Analysis in N_2 Atmosphere (Heating rate 20°C/min)

Sample Designation	T_i (°C)	T_{max} (°C)	T_f (°C)	% Weight Loss at 500°C
POI-100	301	395	450	93
POI-125	367	430	456	96
POI-150	366	420	454	94
POI-175	365	415	456	95
POI-200	370	425	458	94
POI-100(60)	367	430	456	96
POI-100(70)	327	420	450	96
POI-100(80)	348	419	451	97

Thermal stability of the copolymer was determined by recording TG/DTG traces in nitrogen atmosphere. The relative thermal stability of the copolymers was compared by comparing the initial decomposition temperature (T_i), temperature of maximum rate of weight loss (T_{max}), final decomposition temperature (T_f) and percent weight loss at 500 °C. All the copolymers were stable upto 300± 5°C. An increase in T_i and T_{max} was observed with increasing concentration of initiator. A decrease in molecular weight was observed (Table 4.) however increase in these temperature is unexpected. This could be due to the change in copolymer composition which can be calculated by taking ^{1}H-NMR.

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