Studies on high conversion polymerization of n-alkyl acrylates

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The effect of initiator [I] and monomer [M] concentration on the molecular weight and molecular weight distribution in behenyl acrylate polymerization is presented. Gel formation was observed at high [I] and [M]. The effect of solvents in the polymerization of behenyl, octadecyl and butyl acrylates is discussed. The gel effect is prominent in non-polar solvents and in solvents with lower transfer constants. The viscosity of the reaction medium appears to control the polymerization rate and molecular weight distribution.

(Keywords: alkyl acrylates; polymerization; molecular weight distribution)

INTRODUCTION

Homopolymers of alkyl acrylates and methacrylates and their copolymers with ethylene, vinyl acetate, etc. are used extensively as pour-point depressants and flow improvers in high waxy crude oils, lubricating oils and fuel oils. The alkyl chain length in these polymers is usually more than 14 carbons. Behenyl acrylate (BeA), a mixture of C_{22}, C_{20} and C_{18} acrylates, is used extensively in the preparation of these additives. The molecular weight (MW) and molecular weight distribution (MWD) of the polymers are important in the performance of these additives, particularly for crude oils. Although a number of patents describe the preparation of these additives, kinetic studies are very few. Vinyl polymerizations are complicated by the Tromsdorff effect, commonly referred to as the gel effect. The gel effect occurs due to the decreased mobility of polymer chain radicals with increasing viscosity of the medium. A number of workers[1-6] have reported higher than first order dependence on monomer concentration, [M], although the initiator order was 0.5 in the alkyl acrylate polymerization. From our studies[7] and the reports of Scott and Senogles[5,8], it appears that the monomer order increases and initiator order decreases as the length of the alkyl chain is increased. The overall rate constant decreases and the activation energy increases as the alkyl chain is increased. We have shown that the gel effect is also responsible for deviations in the kinetic orders, even at low conversions.

When the polymerization is carried to higher conversions, the MW and MWD show considerable changes due to the changes in kinetic values. With the decrease in [M] and initiator concentration, [I], as the conversion increases, the propagation rate constant (k_p) and termination rate constant (k_t) are affected differently. The MW depends to a considerable extent on the ratio $[M]/[I]^{1/2}$. With [I] decreasing faster than [M] with increasing conversion, the MW increases considerably and MWD may become broader at higher conversions. When the gel effect is pronounced, it results in further broadening of MWD. Branching reactions in the polymerization also lead to broadening of MWD.

In the present study we report the polymerization of BeA with special reference to MW development. The effect of solvents in the polymerization is also reported for BeA, n-butyl acrylate (BA) and n-octadecyl acrylate (OA).

EXPERIMENTAL

The preparation of OA and the purification of BA, OA and BeA have been reported in earlier publications[7,9]. The commercial BeA used in the polymerization is a mixture of n-octadecyl (14.8%), n-eicosyl (15.1%) and n-docosyl (70.1%) acrylates. The solvents and the initiator, benzoyl peroxide (BP), were purified by standard methods. The percentage conversion was determined gravimetrically and dilatometrically. MW was determined with a Waters g.p.c. unit using 10^6, 10^5, 10^4 and 500 Å columns in series. Samples were eluted with tetrahydrofuran at a flow rate of 1 ml min^{-1}. Seven narrow MWD polystyrene standards (Waters) with MW ranging from 1.8×10^6 to 2100 were used for calibration.

RESULTS AND DISCUSSION

The results of polymerization of BeA in toluene at 70°C with different [I] and [M] are presented in *Table 1*. The conversion was very low at lower [I]. At higher [I], the $\bar{M}_w$ increased with increasing conversion. The $\bar{M}_n$ increased up to 60% conversion and then decreased with further increase in conversion. Increase in [I] resulted in gel formation at above 80% conversion. At still higher [I], the gel formation was observed at lower conversion. The decrease in $\bar{M}_n$ could be due to termination by transfer to solvent and/or disproportionation in addition to combination. The $\bar{M}_w$ above 60% conversion did not show significant change. Higher [I] resulted in higher

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Table 1 Effect of [I] and [M] on MW in the polymerization of behenyl acrylate (solvent = toluene, temperature = 70°C)

[M] (mol dm^{-3})	[I] × 10^3 (mol dm^{-3})	Time (min)	Conversion (%)	$\bar{M}_n$	$\bar{M}_w$	Polydispersity
0.87	1.3	180	8	19000	106000	5.6
0.87	1.3	450	25	23000	116000	5.0
0.87	2.7	40	28	18000	86000	4.8
0.87	2.7	100	65	42000	126000	3.0
0.87	2.7	270	>90	22000	135000	6.1
0.87	5.3	60	65	69000	360000	5.2
0.87	5.3	160	>80	Gel formation		
0.87	7.9	70	>60	Gel formation		
1.75	2.7	100	>70	Gel formation		
0.87	2.7	100	67	39000	119000	3.8
0.45	2.7	100	45	34000	81000	2.4
1.75	1.3	180	40	27000	190000	7.0
0.87	1.3	180	8	19000	106000	5.0

Table 2 Effect of temperature on MW in behenyl acrylate polymerization (solvent = toluene, [M] = 0.87 mol dm^{-3})

[I] × 10^3 (mol dm^{-3})	Temperature (°C)	Time (min)	Conversion (%)	$\bar{M}_n$	$\bar{M}_w$	Polydispersity
2.7	80	100	>90	32000	550000	17.2
1.3	80	100	75	27000	450000	16.7
0.7	80	100	55	31000	106000	3.4
2.7	100	100	>85	24000	31000	1.3
5.3	100	15	30	19000	30000	1.6
5.3	100	100	>90	14000	27000	1.9
7.9	100	100	>90	12000	23000	1.9
10.6	100	100	>90	9300	21000	2.3
13.2	100	100	>90	5000	17000	3.4
13.2	100	15	50	7000	22000	3.1

MW at higher conversion. As [M] increased, the MW increased at all conversions. With increasing [M], gel formation was observed at lower conversions. With increasing conversion and MW, branching reactions appear to have predominated resulting in gel formation. It appears that the viscosity of the polymerizing medium influenced the termination at higher conversions. Griffiths *et al.*[10] have shown that increasing the alkyl chain length in alkyl methacrylate polymerization increases the branching reactions. The gel effect and branching reactions could have contributed to gel formation in the BeA polymerization.

The results of polymerization in toluene at 80 and 100°C are presented in *Table 2*. Unlike polymerization at 70°C, gel formation was not observed in toluene at 80°C, even at higher [I]. However, the solubility of the product obtained at above 80% conversion was poor in hydrocarbon solvents, which indicates a high degree of branching. The reproducibility of MW was relatively poor at above 60% conversion. The absence of gel formation at 80°C polymerization in toluene indicates that termination by disproportionation and transfer to solvent was higher and branching reactions lower in comparison to 70°C polymerization. It appears that below a critical radical chain length, the transfer reactions and disproportionation play a significant role.

The results of polymerization at 100°C indicate that disproportionation and transfer to solvent play a major role in view of the lower viscosity at higher temperature. In some of the experiments, bimodal MW peaks are obtained, indicating termination by different mechanisms. With increasing conversion at 100°C a considerable decrease in MW was noticed, which could have arisen only as a result of increasing termination by disproportionation. At lower conversion, the termination by combination appears to be dominant whereas at higher conversion the termination by disproportionation is considerable. The g.p.c. analysis of some products indicates that at lower conversion, unimodal peaks, and at higher conversion, bimodal MW peaks are obtained (*Figure 1*).

Polymerization was carried out in different solvents to determine the effect of transfer constant on polymerization of BeA. The transfer constants for polymerization of higher acrylates are not available in the literature so the constants for ethyl acrylate[11] are shown in *Table 3*, along with the viscosity of BeA in different solvents. The results of polymerization in different solvents are presented in *Table 4*. Gel formation occurred for polymerization in benzene and heptane at above 50% conversion. The polymers obtained by polymerization in benzene have slightly higher MWs. In xylene and carbon tetrachloride (CCl_4), gel formation was not observed even at higher conversions (>80%). The MW, particularly $\bar{M}_n$, in CCl_4

polymerization appears to be higher, which could be due to the higher initial viscosity of the reaction medium. The difference in $\bar{M}_n$ in heptane and CCl_4 polymerization is not significant, in spite of the higher transfer constant for CCl_4. Gel formation in benzene occurred at lower conversion and with lower [I] than in toluene. The gel formation for 80°C polymerization in benzene occurred at lower conversion than in 70°C polymerization. These results suggest that the high initial rate of polymerization leads to gel formation. With the decrease in termination due to the gel effect, branching reactions may predominate, and with the increase in viscosity of the polymerizing medium with increasing conversion, transfer to solvent also appears to decrease. These results suggest that increasing viscosity of the polymerizing medium determines the course of polymerization.

The percentage conversion with time for polymerization of BA and OA in these solvents is presented in *Figures 2* and *3*, respectively. In polymerization in benzene and heptane, which have lower transfer constants, the rate of polymerization (R_p) increased with time even up to 30% conversion, whereas R_p decreased with time in toluene and xylene. The gel effect was indicated in benzene and heptane. More polar solvents showed higher initial R_p. In the case of CCl_4, the high initial R_p could be partly due to the higher initial viscosity.

Table 3 Ethyl acrylate transfer constants[11] and viscosity of behenyl acrylate

Solvent	Temperature (°C)	Constant, $C_S \times 10^4$	Behenyl acrylate ([M]=0.87 mol dm^{-3}) viscosity × 10^3 (Pa s)
Benzene	60	0.27	
	80	0.525	
	25	-	1.53
Hexane	60	0.593	
	80	0.97	
Toluene	70	1.84	
	80	2.60	
	100	6.80	
	25	-	1.59
CCl_4	70	1.13	
	80	1.55	
	25	-	2.5
Xylene	25	-	1.65
Heptane	25	-	1.36

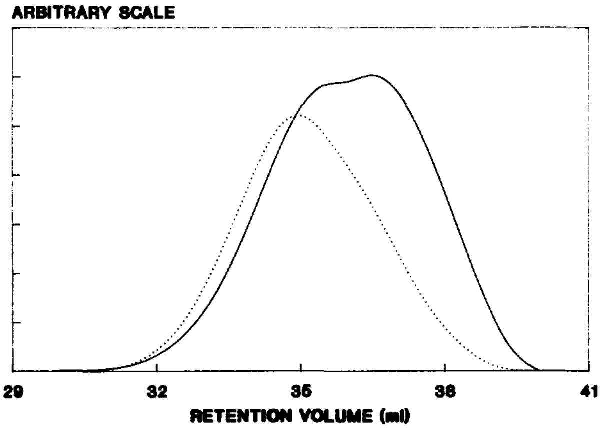

Figure 1 G.p.c. curves of poly(behenyl acrylate) at different conversions with [M]=0.87 mol dm^{-3} and [I] (BP)=5.3×10^{-3} mol dm^{-3} at 100°C in toluene: ...., 30% conversion; ——, 90% conversion

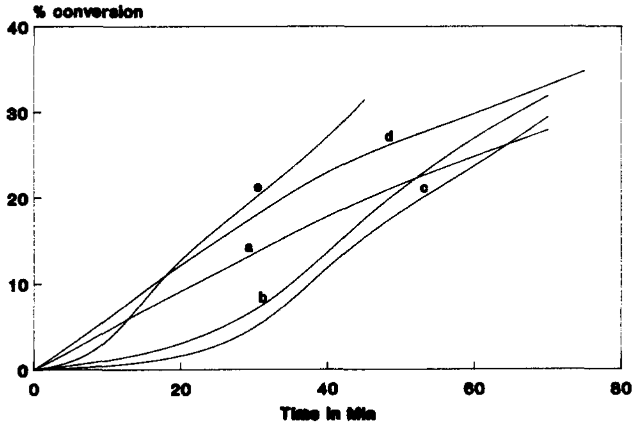

Figure 2 Plot of percentage conversion against time for n-butyl acrylate polymerization at 70°C in different solvents: (a) xylene, (b) benzene, (c) heptane, (d) toluene and (e) carbon tetrachloride. [M]=1.30 mol dm^{-3}, [I] (BP)=3.36×10^{-3} mol dm^{-3}

Table 4 Effect of solvent on MW in behenyl acrylate polymerization ([M]=0.87 mol dm^{-3})

Solvent	Temperature (°C)	[I]×10^3 (mol dm^{-3})	Conversion (%)	$\bar{M}_n$	$\bar{M}_w$	Polydispersity
Benzene	70	1.4	30	81000	137000	1.7
	70	2.7	35	85000	436000	5.1
	70	2.7	>60	Gel formation		
	70	5.3	>50	Gel formation		
Heptane	70	2.7	50	71000	350000	4.9
	70	2.7	>65	Gel formation		
Xylene	70	2.7	60	23600	47000	2.0
	70	5.3	85	18000	42000	2.3
CCl_4	70	2.7	80	64000	160000	2.5
Benzene	80	0.7	35	57000	320000	5.6
	80	1.4	35	62000	125000	2.0
	80	1.4	>75	Gel formation		
	80	2.7	>65	Gel formation		
	80	5.3	>50	Gel formation		

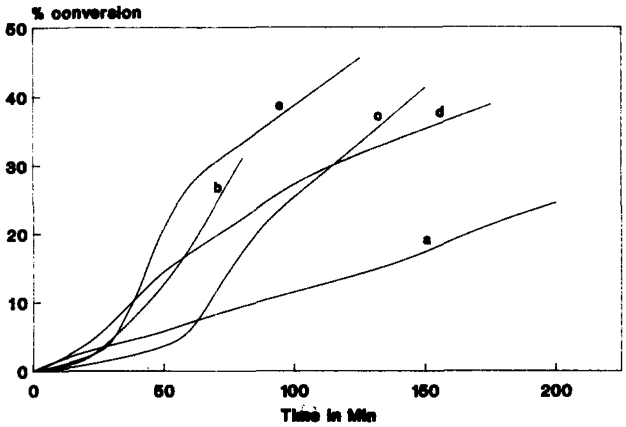

Figure 3 Plot of percentage conversion against time for n-octadecyl acrylate polymerization at 70°C in different solvents: (a) xylene, (b) benzene, (c) heptane, (d) toluene and (e) carbon tetrachloride. $[M]=0.98\ \text{mol dm}^{-3}$, $[I]$ (BP)$=2.61\times10^{-3}\ \text{mol dm}^{-3}$

Table 5 Effect of solvents on MW in butyl and octadecyl acrylate polymerization (temperature = 70°C)

Solvent	Conversion (%)	$\bar{M}_n$	$\bar{M}_w$	Polydispersity
n-Butyl acrylate polymerization[a]				
Benzene	32	79 000	210 000	2.7
Heptane	30	57 000	170 000	3.0
CCl_4	31	54 000	110 000	2.0
Toluene	45	53 000	83 000	1.6
Xylene	30	34 000	48 000	1.4
n-Octadecyl acrylate polymerization[b]				
Benzene	30	55 000	160 000	2.9
Heptane	45	37 000	140 000	3.8
CCl_4[c]	44	19 000	60 000	3.2
Toluene	40	22 000	81 000	3.7
Xylene	30	20 000	40 000	2.0

[a] $[M]=1.30\ \text{mol dm}^{-3}$, $[I]=3.36\times10^{-3}\ \text{mol dm}^{-3}$
[b] $[M]=0.98\ \text{mol dm}^{-3}$, $[I]=2.61\times10^{-3}\ \text{mol dm}^{-3}$
[c] Higher $[I]$ of $3.42\times10^{-3}\ \text{mol dm}^{-3}$ was used

The R_p in CCl_4 polymerization did not show significant change up to 30% conversion in BA polymerization. The MW data are presented in *Table 5*. The polydispersity was higher in benzene and heptane. Polymerization of OA in toluene also gave a higher polydispersity, probably because of the initial gel effect, as indicated in the conversion *versus* time plot. Sato *et al.*[12] have suggested that the initiation rate in polar solvents is higher than in non-polar solvents, and that R_p decreases with increasing polarity of the solvent whereas k_t is not influenced so much by the solvents. They have also suggested that values of R_p and MW of the polymer are lower in the case of more polar solvents. In our studies on acrylate polymerization, the MW was lower in more polar solvents. R_p was initially high in more polar solvents and decreased with time, whereas in less polar solvents R_p increased with time due to the gel effect. It appears that in alkyl acrylate polymerization, the viscosity of the polymerizing medium, transfer to solvent, branching and gel effect affect the rate of polymerization. In view of the complexity of the polymerization with higher [I] and [M], the reproducibility and repeatability of the MW at higher conversions appears to be in question. We have observed that with high [I] and [M] at high conversions (>60%), the variation in MW was more than 30%, particularly for $\bar{M}_w$ in some experiments. The percentage conversion also varied by more than 10%.

CONCLUSIONS

At higher [I] and [M], branching reactions lead to gel formation in behenyl acrylate polymerization. Termination by disproportionation and/or transfer to solvent below a critical radical chain length appeared to be significant at higher conversions. The gel effect was prominent in solvents with low transfer constants and in non-polar solvents. Viscosity of the polymerizing medium influenced the high conversion polymerization in alkyl acrylate polymerization.

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