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Studies in Transesterification. VII. Thermally Stable Surface Graft Catalysts *

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ABSTRACT

The preparation of methacrylate esters by transesterification with thermally stable surface or shell graft resins as acidic catalysts and n-butanol, n-hexanol, and n-tridecanol as the reactant alcohols is described. The performance of resins with a reactive shell graft polymerized to a solid polyethylene or polytrifluorochloroethylene nucleus has been compared with several conventional micro and macroporous cation exchangers. The graft polymers exhibit faster reaction rates than micro- and macroporous resins of significantly higher capacity. The graft polymer employing a polyethylene nucleus is of similar thermal stability to the conventional cation exchangers, while the second type of graft polymer exhibits increased thermal stability which allows repeated use at the operating temperatures experienced.

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INTRODUCTION

The use of cation exchangers as acidic catalysts in the transesterification of acrylic esters has been reviewed [1, 2], and a surface graft resin has been reported for the synthesis of n-butyl methacrylate in which a more rapid reaction was achieved than with two conventional microporous cation exchangers (Zeo-Karb 225 and Dowex 50W-X8) of substantially higher capacity [3]. The conventional resins showed significant thermal breakdown between 110 and 120°C and were not suitable for repetitive use, while the graft polymer which employed a polyethylene nucleus performed essentially identically in successive experiments at these temperatures.

While the microporous ion exchangers used previously as controls have been widely employed as catalysts [4] in a variety of low temperature syntheses, the materials were developed primarily for use as cation exchangers in aqueous media. In a further examination of surface graft catalysts, available macroporous exchangers developed as catalysts for synthesis in organic systems have been considered.

The present work describes the preparation and application as catalysts of a reactive surface graft-polymerized onto polyethylene and onto trifluorochloroethylene as a more thermally stable nucleus which provides a resin more resistant to thermal degradation and thus allows transesterification reactions to be carried out at higher temperatures suitable for the synthesis of higher alkyl methacrylate esters. The reaction rates and the influence of equilibrium capacities of the catalysts are described.

EXPERIMENTAL

Ion-Exchange Catalysts

The graft polymer having a polyethylene nucleus was prepared according to the following procedure [5-7].

Into a 2000-ml flanged flask fitted with a stirrer, gas inlet tube, heating coil, and condenser was charged 200 g of spherical polyethylene particles [8]. Styrene, stabilized with 0.2% of its weight of hydroquinone, was then added in quantity sufficient to cover the particles. The contents of the flask were stirred and purged with nitrogen for 30 min, before heating to 29°C and irradiation from a cobalt-60 source at a dose rate of 1.7×10^5 rad/hr until the dose of 0.5 Mrad was delivered. At the completion of the irradiation, the product was separated by filtration, washed with benzene until free of extractable homopolymer, leached with methanol over a period of 16 hr, filtered,

and dried under vacuum at 60°C for 72 hr. The degree of grafting achieved expressed in parts by weight of the outer polymeric shell per 100 parts of complete particle is 15%. The presence of polystyrene in the product was confirmed by infrared spectroscopy and the formation of a discrete shell of polystyrene surrounding the nucleus was confirmed by microscopy [9].

The 150 g portion of particles obtained was immersed in 100 g of chlorosulfonic acid and heated with stirring at 60-70°C until no more hydrochloric acid was liberated. The mixture of particles was then poured into 30% sulfuric acid and filtered. The particles were then successively poured into 10% and 3% sulfuric acid and filtered each time from the liquid. The particles were then recovered by filtration and thoroughly washed with water. There was thus obtained a sulfonated cation-exchange resin in particle form which had an equilibrium capacity of 1.21 meq/g. The mesh size of the catalyst was 22-36 BSS.

The catalyst having a trifluorochloroethylene nucleus was prepared by the following procedure. Polytrifluorochloroethylene powder (Kel-F, 250 g) was sieved through a 10-mesh BSS sieve and transferred to a 2000-ml cylindrical glass reaction vessel. Styrene monomer (500 ml) which had been distilled under reduced pressure in an atmosphere of nitrogen was added to the polytrifluorochloroethylene and the mixture was freeze-degassed three times at a pressure of 0.01 Torr, liquid nitrogen being used as coolant. The reaction vessel was placed at the center of a circular arrangement of eight 250-C: cobalt-60 γ -emitter radiation sources. Irradiation was carried out at ambient temperature for 3 hr, during which the dose rate in the reaction vessel was maintained at 1.75×10^5 rad/hr. The reaction mixture was then filtered and washed with hot benzene until free of homopolymerized styrene. The weight of the irradiated product after drying in vacuo at 60°C was 269.8 g, and the degree of grafting expressed as parts by weight of the graft per 100 parts of complete particle was 40%. The presence of polystyrene in the graft copolymer was determined as outlined above.

The particles were sulfonated and recovered as previously outlined, and a sulfonated cation-exchange resin was produced in particle form with an equilibrium capacity of 2.7 meq/g. Other resins were similarly prepared with capacities of 1.1 and 0.2 meq/g.

Dowex 50W-X8 (8% crosslinking, Dow Chemical Co., Michigan) and Zeo-Karb 225 (12% crosslinking, Permutit Co., London), each similar unfunctional cation exchangers of the strongly acidic type with active SO₃H groups on a microporous styrene-divinylbenzene copolymer with exchange capacities of 5.1 and 4.5-5.0 meq/g, respectively, were used together with Amberlite 200 and Amberlyst 15 (Rohm and Haas, Philadelphia). Amberlite 200 is a macroporous ion exchanger based on styrene-divinylbenzene, particle size BSS 40-45 mesh and capacity 3.46 meq/g. Amberlyst 15 is another

TABLE 1. Reaction Rates for n-Hexanol Transesterification

Conversion to ester (%)	Polyethylene (capacity 1.21 meq/g), time (hr)		Kel-F (capacity 2.7 meq/g) time (hr)	
	Run 1	Run 2	Run 1	Run 2
0	-	-	-	-
20	0.37	0.52	0.28	0.30
40	0.72	1.06	0.58	0.56
60	1.08	1.62	0.97	0.96
80	1.52	2.12	1.40	1.44
90	1.78	2.33 ^a	1.75	1.72

^a86.0%.

macroreticular ion exchanger of the strongly acidic type designed for use with organic media; a fraction of particle size 16-50 mesh BSS and capacity of 4.9 meq/g was used.

Preparation of Esters

Butyl Methacrylate. Methyl methacrylate (2.0 moles) inhibited with 1% p-tert-butyl catechol and n-butanol (1 mole) were charged into a reaction vessel containing 43.5 g surface graft catalyst (25% based on 1 mole of each reactant). The catalyst was used in the acid form.

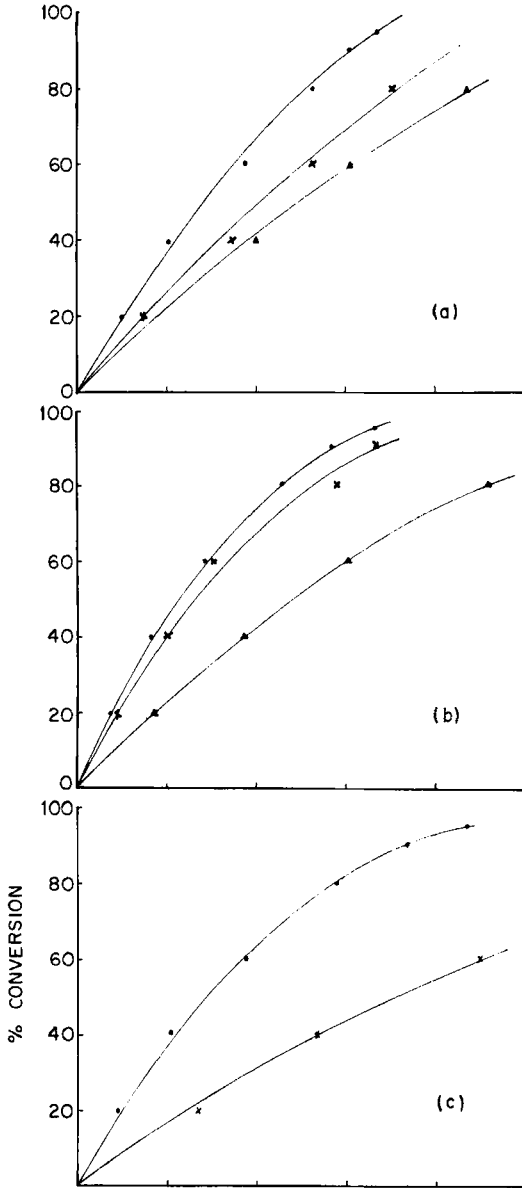
The reaction vessel employed an anchor-type stirrer and was fitted with a 12 in. fractionating column. The collection rate of the methyl methacrylate methanol azeotrope was controlled by a temperature sensitive still head such that the maximum temperature of collection did not exceed 66°C. The progress of the reaction was followed by analysis of the distillate and the conversion with time was calculated.

The reaction had proceeded to virtual completion in 2.5 hr. The temperature of the reactants at this time was 121°C, and the catalyst was filtered off for reuse. The n-butyl methacrylate was recovered by fractional distillation. The catalyst, after washing with solvent and drying, was reused five times without apparent deterioration.

The preparation was repeated with the acid form of Dowex 50W-X8 Zeo-Karb 225, Amberlite 200, and Amberlyst 15, each in the same

TABLE 2. Comparative Reaction Rates for n-Butyl Methacrylate Synthesis

Catalyst	Conver- sion (%)	Time (hr)				
		Run 1	Run 2	Run 3	Run 4	Run 5
Kel-F (25% catalyst) (capacity 2.7 meq/g)	0	-	-	-	-	-
	20	0.50	0.40	0.40	0.40	0.45
	40	1.00	0.80	0.85	0.80	0.90
	60	1.45	1.20	1.30	1.25	1.35
	80	2.05	1.70	1.85	1.75	2.10
	90	2.35	2.05	2.20	2.10	2.40
	95	2.55	2.25	2.40	2.35	2.55
Dowex 50W8 (25% catalyst) (capacity 5.1 meq/g)	0	-	-	-	-	-
	20	0.50	0.7	0.7	-	-
	40	1.00	1.7	1.9	-	-
	60	1.85	2.6	3.1	-	-
	80	2.70	3.5	4.3	-	-
	90	3.10	4.3	-	-	-
	95	3.30	-	-	-	-
Zeokarb 225 (30% catalyst) (capacity 4.5- 5.1 meq/g)	0	-	-	-	-	-
	20	0.35	0.45	0.85	-	-
	40	0.80	0.95	1.80	-	-
	60	1.40	1.50	3.00	-	-
	80	2.30	2.90	4.60	-	-
	90	2.80	3.30	-	-	-
	95	3.30	-	-	-	-
Amberlite 200 (25% catalyst) (capacity 3.46 meq/g)	0	-	-	-	-	-
	20	0.45	1.35	1.35	1.40	-
	40	1.06	2.76	2.65	3.40	-
	60	1.85	4.45	4.25	5.15	-
	80	2.85	-	-	-	-
	90	3.65	-	-	-	-
	95	4.30	-	-	-	-
Amberlyst 15 (25% catalyst) (capacity 4.09 meq/g)	0	-	-	-	-	-
	20	0.72	0.60	1.04	-	-
	40	1.35	1.40	2.00	-	-
	60	2.12	2.40	3.15	-	-
	80	3.00	4.00	-	-	-
	90	3.60	-	-	-	-
	95	-	-	-	-	-



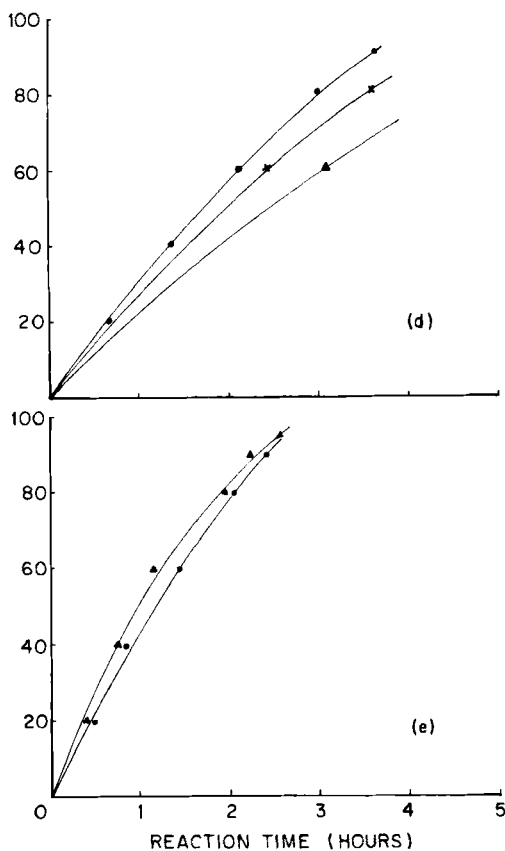


FIG. 1. Reaction rates for repetitive experiments with (a) Dowex 50W-X8 (25% w/w), (b) Zeo-Karb 225 (30% w/w), (c) Amberlite 200 (25% w/w), (d) Amberlyst 15 (25% w/w), and (e) Kel-F graft, capacity 2.7 meq/g (25% w/w as catalyst in the synthesis of n-butyl methacrylate: (●) first experiment; (×) second experiment; (△) third experiment.

proportion by weight (except Zeo-Karb 225 where the resin was increased to 30% by weight). With the first three resins, the reactions reached 95% completion in 3.30 and 4.30 hr, respectively after which the catalysts were recovered for repetitive reactions. The Amberlyst 15 reached 90% completion in 3.60 hr, after which the catalyst was recovered for reuse.

Tridecyl Methacrylate. The procedure for producing n-butyl methacrylate was carried out with tridecanol in place of n-butanol and the Kel-F cored catalyst as recovered from the experiments with n-butanol was used at the same level. The reaction continued essentially to completion in 1.75 hr, and a reaction temperature of 138°C was recorded. There was no apparent deterioration of the catalyst as the experiment was repeated with virtually identical results.

n-Hexyl Methacrylate. The procedure for producing n-butyl methacrylate was repeated with n-hexanol in place of n-butanol using both the polyethylene and Kel-F catalysts each at the 25% level. The reaction had reached virtual completion in 2 hr. During the course of the reaction the reactants were heated to 135-140°C.

RESULTS AND DISCUSSION

While the stability of a surface graft catalyst having a polyethylene nucleus and the decomposition of two microporous ion exchangers has been demonstrated [3], with the synthesis of n-butyl methacrylate at operating temperatures of 120°C it is evident that the graft is destroyed at higher temperatures. Table 1 shows the use of catalysts with both substrates with the transesterification of n-hexanol. With a polyethylene substrate it was evident that some decomposition of the catalyst had occurred, as the reactants and azeotrope collected possessed a strong characteristic sulfurous odor due to the decomposition of some of the sulfonic acid groups, indicating that the graft was disintegrating. There was also some degradation of the catalyst core.

Catalytic activity was shown in the first run, despite decomposition of the catalyst as the catalytic groups were simply transferred from a recoverable solid matrix into solution with the reactants. On repeated use after washing free of soluble sulfonic acid, a reduced rate of conversion was observed. Further deterioration of the catalyst occurred due to liberation of sulfonic acid, and a subsequent reaction would be even slower.

Decomposition of the catalyst with solution of catalytic groups is most undesirable, as the utility of removing the catalyst from the reactants is lost and further purification of the mixed reactants is necessary.

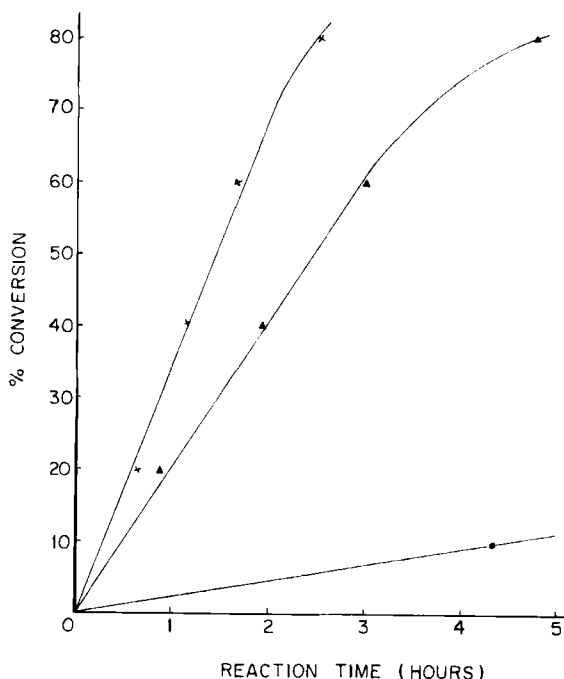


FIG. 2. Reaction rates with Kel-F graft catalysts with various capacities in the synthesis of n-butyl methacrylate: (a) 2.7 meq/g; (b) 1.1 meq/g; (c) 0.2 meq/g.

With the Kel-F graft (fresh) catalyst, the reaction with n-butanol proceeded to virtual completion in 2 hr, while repetitive reactions with the recovered catalyst proceeded at essentially identical rates at reaction temperatures which reached 140°C.

Table 2 shows reaction times and conversions obtained with n-butanol for each of the catalysts, where it is apparent that a rapid decrease in catalytic activity occurs with use with all four of the proprietary ion exchangers, the performance of the macroporous resins being considerably poorer than for the older microporous types. The Kel-F graft (capacity 2.7 meq/g) was seemingly unaffected by the temperatures experienced, the rate of the fifth repetitive experiment being essentially identical with the initial experiment. A plot of the repetitive reaction rates is shown in Fig. 1.

The reaction rates of the surface graft are substantially greater than for the porous ion exchangers particularly when the lower capacities are considered, and this enhanced catalytic activity has been

discussed previously by Battaerd and Suidak [9] in their early work, which reported the development of this type of surface graft polymer.

With shell graft resins it has been shown [9] that fast exchange rates do not depend on small particle sizes although, as might be expected, the rates are dependent on the capacities, as shown in Fig. 2, where resins of similar size (60-68 BSS) and increasing capacity are considered.

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REFERENCES

- [1] J. K. Haken, Synthesis of Acrylic Esters by Transesterification, Chemical Process Monograph Series, Noyes Development Corp., New Jersey, 1967.
- [2] R. Sridharan and I. M. Mathia, J. Sci. Ind. Res., **33**, 178 (1974).
- [3] J. K. Haken and D. K. M. Ho, J. Appl. Chem., **20**, 101 (1970).
- [4] K. C. Ooesterhout, Thesis Ph.D., Penn. State Univ., 1967.
- [5] H. A. J. Battaerd and I. C. I. A. N. Z. Ltd., Austral. Pat. 422,536.
- [6] H. A. J. Battaerd and I. C. I. A. N. Z. Ltd., Austral. Pat. 425,620.
- [7] J. K. Haken, D. K. M. Ho, and Unisearch Ltd., Austral. Pat. 454,792.
- [8] H. A. J. Battaerd and I. C. I. A. N. Z. Ltd., U. S. Pat. 3,504,434.
- [9] H. A. J. Battaerd and R. Suidak, J. Macromol. Sci.-Chem., **A4**, 1259 (1970).

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