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A Simple Method for the Determination of the Degree of True Grafting in Graft Copolymerization of a Vinyl Monomer on Cellulose or Oxycellulose

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A B S T R A C T

Graft copolymerization of methyl methacrylate (MMA) on cellulose or oxycellulose gave a gross polymer product from which the free poly(methyl methacrylate) (PMMA) was easily separated by extraction with benzene. From the residue called the apparent graft copolymer, the unbound or free cellulose/oxycellulose portion was separated from the cellulose/oxycellulose-PMMA graft copolymer portion by extracting the former with 4% aqueous NaOH following a xanthation process. The xanthation method allowed easy determination of efficiency of grafting with respect to cellulose/oxycellulose and degree of true grafting giving mmoles or moles of PMMA grafted per gram or per mole of cellulose/oxycellulose.

I N T R O D U C T I O N

When a vinyl monomer is polymerized in the presence of cellulose, the gross product obtained usually consists of three different polymeric

entities, viz., free or unbound vinyl polymer, cellulose-vinyl graft copolymer, and free cellulose [1]. In almost all cases it is easy to isolate the free vinyl polymer by an appropriate selective extraction process but thereafter it is difficult if not impossible to separate the free or ungrafted cellulose portion from the true graft copolymer fraction in the residue, which may be commonly termed as the apparent graft copolymer system because of the general insolubility of cellulose. Most reports on graft copolymerization of cellulose therefore give little information on the extent, efficiency, or degree of true grafting with respect to cellulose [2-5]. The present paper reports results of our investigations on this problem, based on selective extraction of free cellulose from the apparent cellulose-vinyl graft copolymer.

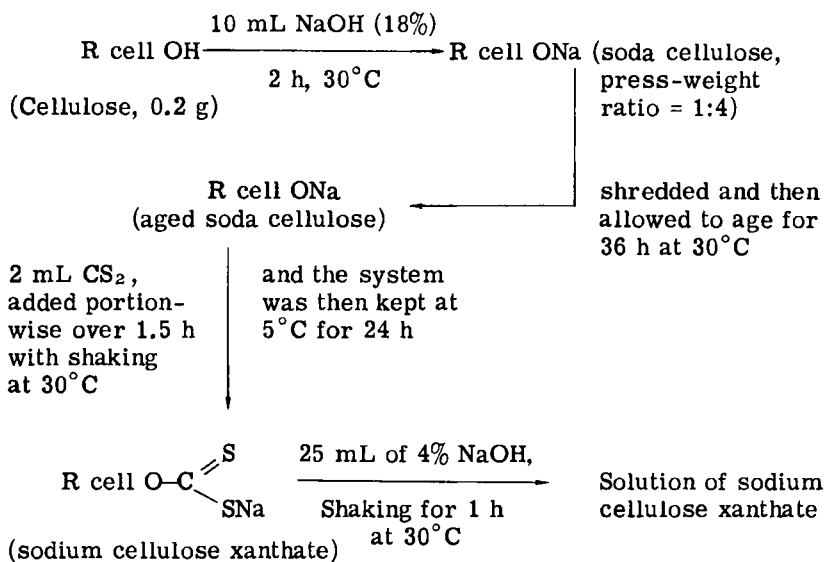
EXPERIMENTAL

Methyl methacrylate (MMA) was used as the monomer in the present studies, and it was purified following standard procedures. Cellulose or oxycellulose (prepared by periodate treatment of cellulose under conditions that effect practically no chain degradation [1]) was used as the preformed polymer for graft copolymerization, and the initiators used were 1) the KMnO_4 -oxalic acid redox system or 2) $\text{K}_2\text{S}_2\text{O}_8$ in limited aqueous systems under photoactivation with visible light at a low temperature ($32 \pm 1^\circ\text{C}$). Experimental details have been given elsewhere [1, 2]. In each case the polymerization product, called the gross polymer, was isolated, dried, weighed, and then subjected to selective extraction of the free poly(methyl methacrylate) (PMMA) fraction with benzene according to procedures already given [1]. The residue after this first extraction step, called the apparent graft copolymer, was then subjected to a xanthation process so as to enable selective extraction of the free cellulose/oxycellulose fraction.

Xanthation

It is well known that cellulose can be easily xanthated by following the reaction steps given on the following page [6].

Xanthated cellulose formed as above was completely soluble in 4% aqueous NaOH solution. A known weight of cellulose (0.2-0.3 g) was then intimately mixed with 100 to 1000% its weight of PMMA in benzene solution and the PMMA was then completely precipitated out with excess petroleum ether. The mixed polymer system, collected and dried at 40°C in vacuum, was then subjected to the xanthation procedure whereby the cellulose portion of the mixture was completely solubilized in 4% aqueous NaOH solution, and the PMMA portion, remaining practically unaffected, was quantitatively isolated on



decantation, filtration, washing with dilute NaOH solution and distilled water, and finally drying.

The residual mixed polymer system (apparent graft copolymer), obtained after benzene extraction of each of several gross polymer samples prepared by graft copolymerization of cellulose or oxycellulose and MMA [1, 2], was then subjected to the above procedure of xanthation. The product after xanthation when extracted with 4% aqueous NaOH solution is expected to produce a solution of the free cellulose/oxycellulose fraction leaving the true cellulose/oxycellulose-PMMA graft copolymer as a partially swollen residue. In fact, in each case it was found that a significant portion of the mixed polymer system (apparent graft copolymer) dissolved when the respective xanthated product was shaken well with 4% aqueous NaOH solution. The residue was then isolated by filtration, washing thoroughly and successively with 4% NaOH solution, 0.5 N HCl solution, and distilled water, and finally drying at 40°C under vacuum. Loss in weight due to dissolution of free cellulose/oxycellulose was noted, and grafting efficiency (%) on the basis of cellulose/oxycellulose was calculated. The final residual polymer is referred to as the true graft copolymer. Grafting efficiency (%) with respect to total PMMA formed, E_M , was also easily calculated after the benzene-extraction step on the basis of relevant data giving amounts of total PMMA formed and free and bound PMMA [1, 2].

The molecular weight of the cellulose used was determined viscometrically following nitration of the cellulose according to the method of Alexander [7]. The grafted-on PMMA chains were freed from associated cellulose or oxycellulose/(bound/unbound) by treating

TABLE 1. Determination of True Grafting in the Graft Copolymerization of Cellulose or (Oxy)cellulose and MMA at $30 \pm 1^\circ\text{C}$ in Limited Aqueous Systems.^e Molecular Weight of Cellulose Used: 9.52×10^5

Expt.	Copper number of cellulose	Time of graft copolymerization (h)	% Grafting achieved	Apparent graft copolymer, w ₁ (g)	PMMA in		Mol. wt. of grafted PMMA, $\bar{M}_n \times 10^{-5}$
					w ₁ (g) apparent graft copolymer, w ₂ (g)	w ₂ (g)	
I. ^a Initiator: Aqueous KMnO ₄ -Oxalic Acid Redox System ^c under Photoactivation with Visible Light							
1	0.25	1.5	75.80	0.3802	0.1641	0.1641	14.55
2	0.25	3.0	131.30	0.3510	0.1992	0.1992	17.34
3	0.25	6.0	188.67	0.3400	0.2220	0.2220	27.54
4	27.94	1.5	98.95	0.3895	0.1937	0.1937	11.60
5	27.94	6.0	204.80	0.3718	0.2498	0.2498	20.14
6	27.94	3.0	250.30	0.4000	0.2858	0.2858	20.84
II. ^b Initiator: Aqueous K ₂ S ₂ O ₈ ^d under Photoactivation with Visible Light							
7	27.94	1.5	25.00	0.2281	0.0465	0.0465	4.81
8	27.94	6.0	175.00	0.3752	0.2384	0.2384	12.76
9	27.94	7.5	440.30	0.3798	0.3095	0.3095	30.62

(continued)

TABLE 1 (continued)

Expt.	Loss on xanthation, w_3 (g)	Cellulose in true graft copolymer, $(w_1 - w_2 - w_3) = w_4$ (g)	Grafting efficiency (%)		Degree of time grafting	
			With respect to total PMMA formed, E_M	With respect to cellulose taken, E_C	A ^f	B ^g
I. ^a Initiator: Aqueous $KMnO_4$ -Oxalic Acid Redox System ^c under Photoactivation with Visible Light						
1	0.1521	0.0639	76.00	29.59	1.76	1.68
2	0.0633	0.0885	63.30	58.30	1.30	1.24
3	0.0509	0.0671	53.00	56.86	1.19	1.14
4	0.1010	0.0947	50.40	48.39	1.76	1.68
5	0.0433	0.0787	65.10	64.50	1.57	1.50
6	0.0376	0.0766	77.90	67.07	1.78	1.70
II. ^b Initiator: Aqueous $K_2S_2O_8$ ^d under Photoactivation with Visible Light						
7	0.1306	0.0510	100.00	28.08	1.91	1.81
8	0.0476	0.0892	88.00	65.20	2.01	1.99
9	0.0183	0.0519	77.87	73.90	1.94	1.85

^aData obtained from graft copolymerization done according to procedure and set up given in Ref. 1.

^bData obtained from graft copolymerization done according to procedure and set up given in Ref. 2.

^c $KMnO_4 = 0.68$ mg, and oxalic acid = 5.4 mg for Expt. 1-5. For Expt. 6, $KMnO_4 = 1.0$ mg, and oxalic acid = 18.0 mg.

^d $K_2S_2O_8 = 14.45$ mg for Expt. 1, 3-6, and 1.5 mL for Expt. 2.

^eIn each case 0.2 g cellulose (copper number 0.25) or oxycellulose (copper number 27.94) was taken for grafting experiments.

^fA = (mmole of PMMA grafted per gram of cellulose in the true graft copolymer) $\times 10^3$.

^gB = moles of PMMA grafted per mole of cellulose in the true graft copolymer.

the apparent graft copolymer or the corresponding true graft copolymer with 72% H_2SO_4 leading to quick and complete degradation of cellulose chains according to known procedures. The molecular weight of the respective grafted-on PMMA chains, thus isolated free of cellulose/oxy cellulose, was then determined viscometrically from benzene solution [1, 8].

All relevant data are given in Table 1. Calculated values of degree of true grafting in the form of (A) mmoles of grafted-on PMMA per gram of truly grafted cellulose/oxy cellulose and (B) moles of grafted-on PMMA per mole of truly grafted cellulose/oxy cellulose are given in the table. On a mole for mole basis, the true graft copolymers are generally richer in PMMA. It is interesting to note that the average molecular weight of the grafted-on PMMA chains are significantly higher than the average chain length of the cellulose molecules used. This may be understood on the basis of delayed or restricted termination for the grafted-on growing PMMA chains in the cellulose matrix. Variable extents of intermolecular cross-linking of cellulose chains through growing grafted-on PMMA chains as a consequence of such delayed terminations may also partly account for unusually high average chain lengths for the grafted-on PMMA chains in the final analysis.

Obviously, the xanthation technique has its limitations in view of certain side reactions involved in it [6], but it is a simple method for the analysis of cellulose graft copolymer systems of the present kind, providing a reasonably easy determination of extent or degree of true grafting and efficiency of grafting with respect to cellulose (E_c).

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