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Studies in Na-PCMSA-g-PBA: Comparison of Reactivity of Acrylate Monomers towards Photo-Grafting

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Abstract:
In this paper, the reactivity of butyl acrylate (BA) has been compared with that of other acrylate monomers like methyl acrylate (MA) and methyl methacrylate (MMA) towards photo-graft copolymerization of them onto sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA, ($\overline{DS}$ = 1.10). The observed less reactivity of BA compared to that of MA and MMA is explained on the basis of the chemical nature of the monomer(s) as well as on the values of the overall rate of polymerization (R_p). The introduction of carboxymethyl groups in sodium alginate molecules has enhanced its behavior toward photo-grafting of BA onto Na-PCMSA ($\overline{DS}$ = 1.10) for which plausible explanation has been provided.

Keywords: *Monomers, Photo-graft copolymerization, Reactivity of acrylate, Sodium salt of partially carboxymethylated sodium alginate*

Introduction

Chemical modification of polysaccharides (Natural and Renewable) through grafting employing chemical and radiation techniques has received considerable interest in recent years (Bhattacharya & Mishra 2004; Purohit et al. 2023; Setia 2018; Kumar et al. 2017). Among radiation methods, photo-grafting method has several advantages (Trivedi & Chourasia, 2023).

As a part of our research programme, recently we have modified carboxymethylated derivative of sodium alginate i.e. sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA, $\overline{DS}$ = 1.10) by photo-grafting of different vinyl monomers like acrylonitrile (AN) (Trivedi & Chourasia, 2023), methyl acrylate (MA) (Trivedi, Chourasia & Trivedi, 2015), methyl methacrylate (MMA) (Trivedi & Chourasia, 2023) and butyl acrylate (BA) (Trivedi & Chourasia, 2024) onto it using ceric ammonium nitrate (CAN) as a photo-initiator and evaluated one of their potential applications as super absorbents (Trivedi & Chourasia, 2023).

This article is in continuation of our earlier work (Trivedi & Chourasia, 2024) wherein we have reported the optimization of the photo-grafting synthesis of poly(butyl acrylate)-grafted-sodium salt of partially carboxymethylated sodium alginate (Na-PCMSA-g-PBA) through the systematic variation of different reaction conditions in terms of the determination of the highest grafting yields (%G -220.85, %GE = 97.81 and $\%H_p$ = 2.19). The influence of the different reaction conditions on the grafting yields have been discussed and the photo-graft copolymer, Na-PCMSA-g-PBA, has been characterized by employing FTIR, TGA/DTG and SEM techniques. However, the present work reports the comparison of the reactivity of butyl acrylate (BA) (Trivedi & Chourasia, 2024) with that of other acrylate monomers (MA) (Trivedi, Chourasia & Trivedi, 2015) and MMA towards (Trivedi & Chourasia, 2023) photo-grafting and the influence of the introduction of the carboxymethyl group(s) in the sodium alginate molecules on its susceptibility towards photo-grafting of BA onto Na-PCMSA ($\overline{DS}$ = 1.10) using CAN as a photo-initiator.

Materials and Methods

Materials

Materials used in the present work are as discussed in the earlier communication (Trivedi & Chourasia, 2024).

Methods

Carboxymethylation of sodium alginate (Na-PCMSA)

The methods of preparation of Na-PCMSA, its, purification and measurement of the degree of substitution of Na-PCMSA were followed as described earlier (Trivedi & Chourasia, 2024). The $\overline{DS}$ of Na-PCMSA sample was found to be 1.10.

Optimization of the photo-induced synthesis of Na-PCMSA-g-PBA

The photo-induced synthesis of Na-PCMSA-g-PBA was optimized through the variation of different reaction variables as per the experimental procedure discussed earlier (Trivedi & Chourasia, 2024).

Grafted Chains Isolation

For studying the influence of introducing the carboxymethyl groups in SA molecule on the photo-grafting yields, the photo-initiated synthesis of the poly (butyl acrylate) grafted sodium alginate (SA-g-PBA) was carried out using the established optimal reaction conditions in the case of photo-grafting of BA onto Na-PCMSA ($\overline{DS}$ = 1.10) CAN as a photo-initiator (Trivedi & Chourasia, 2024). The experimental procedure followed for the synthesis of SA-g-PBA was the same as discussed earlier (Trivedi & Chourasia, 2024).

Results and Discussion

Grafting yields and Kinetic Parameter

The values of the grafting yields viz. percentage of grafting (%G), percentage of grafting efficiency (%GE), and percentage of homopolymer ($\%H_p$) as well as the kinetic parameter viz. rate of polymerization (R_p) was calculated by using the following equations (Trivedi, Chourasia & Trivedi, 2015; Trivedi & Chourasia, 2024):

$$\%\,G = \frac{\text{Wt. of polymer grafted}}{\text{Initial wt. of backbone}} \times 100 \quad (1)$$

$$\%\,GE = \frac{\text{Wt. of polymer grafted}}{\text{Wt. of polymer grafted} + \text{Initial wt. of backbone}} \times 100 \quad (2)$$

$$\%H_p = 100 - \%GE \quad (3)$$

$$R_p(mol.L^{-1}.s^{-1}) = \frac{\text{Wt. of polymer grafted + Wt. of Homopolymer}}{\text{Mol. wt of monomer x Reaction time (sec) x vol. of the reaction mix (mL.)}} \times 10^3 \quad (4)$$

Comparison of Reactivity of acrylate monomers towards photo-grafting

In order to compare the reactivity of different acrylate monomers, the photo-grafting of MA (Trivedi, Chourasia & Trivedi, 2015; Trivedi & Chourasia, 2023 and BA (Trivedi & Chourasia, 2024) onto Na-PCMSA ($\overline{DS}$ = 1.10) been carried out using CAN as a photo-initiator and the grafting yields were determined under the evaluated respective optimized reaction conditions. The results of the grafting yields are tabulated in Table 1. It becomes evident from the results of this table that reactivity of different acrylate monomers varies towards photo-grafting. All acrylate monomers are not equally reactive towards photo-graft copolymerization. The comparison of the results of the table clearly shows the following reactivity order of monomers:

MA > MMA > BA

Table 1. The values of Grafting yields (%G and %GE) obtained in the case of photo-grafting of MA, MMA and BA on to Sodium alginate (SA) (under optimized reaction conditions[a] derived for Na-PCMSA) as well as Na-PCMSA ($\overline{DS}$ = 1.10).

Structure	Monomer	Grafting Yields		Reference
		%G	%GE	
SA	MA	240.83	86.54	6
	MMA	210.22	87.03	7
	BA	176.18	86.96	8
Na-PCMSA	MA	303.57	98.32	6
	MMA	284.12	98.44	7
	BA	220.85	97.81	8

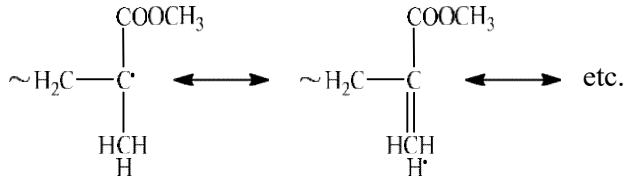
[a]Optimum Reaction Conditions for:

MA: SA/Na-PCMSA (dry basis) = 0.40 g; [CAN] = 6 x 10^{-3} mol/L; [HNO_3] = 0.2 mol/L; [MA] = 0.203 mol/L; Time = 3h; Temperature = 30°C and Total Volume = 150 mL;

MMA: SA/Na-PCMSA (dry basis) = 0.40 g; [CAN] = 4 x 10^{-3} mol/L; [HNO_3] = 0.3 mol/L; [MMA] = 0.152 mol/L; Time = 4h; Temperature = 30°C and Total Volume = 150 mL; and

BA: SA/Na-PCMSA (dry basis) = 0.40 g; [CAN] = 4 x 10^{-3} mol/L; [HNO_3] = 0.3 mol/L; [BA] = 0.152 mol/L; Time = 4h; Temperature = 35°C and Total Volume = 150 mL

The difference in monomer reactivities might depend on solubility, polarity, molecular size, chemical nature etc. With MMA, there is an additional $–CH_3$ group on vinylic carbon position which offer some more steric hindrance than MA. This is why MMA is found to be less reactive than MA. In BA, the ester moiety contains ethyl and n-butyl groups which offers greater steric hindrance towards photo-grafting. The greater reactivity of MMA than BA can also be explained by the fact that the presence of $–CH_3$ group on vinylic carbon in MMA stabilizes the growing grafted polymeric radical by the following resonance structures:



However, no such resonance stabilization is possible for the growing grafted polymeric derived from BA. Secondly, the BA, in the present work, gives less percentage grafting owing to the fact that it easily undergoes monomer transfer reaction leading to the wastage of monomer in side reactions.

Earlier in the case of photo-grafting of MA (Trivedi, Chourasia & Trivedi, 2015); MMA (Trivedi & Chourasia, 2023) and BA (Trivedi & Chourasia, 2024) onto Na-PCMSA using CAN as a photo-initiator, the values of the overall rate of polymerization (R_p) were evaluated, as per Eq.(4), for various acrylate monomer (MA or MMA or BA) concentrations as well as for various photo-initiator (CAN) concentrations. The values of R_p as reported earlier are found to be higher in the case of photo-grafting of MA (Trivedi, Chourasia & Trivedi, 2015) and MMA (Trivedi & Chourasia, 2023) compared to BA (Trivedi & Chourasia, 2024) indicating further that BA is less reactive than MA and MMA towards photo-grafting.

Effect of Introduction of Functional groups in SA molecules

In order to investigate the influence of introducing the functional groups like carboxymethyl in the sodium alginate (SA) molecules on its susceptibility towards photo-grafting of BA, we have carried out the photo-grafting of BA onto SA using the evaluated optimized reactions conditions in the case of photo-grafting of BA onto Na-PCMSA ($\overline{DS}$ = 1.10) (Trivedi & Chourasia, 2024). The results of the grating yields (%G and %GE) are recorded in Table 1. Upon comparing the values of grafting yields, it can be noticed that these values are found to be higher in the case of Na-PCMSA compared to SA. This could be explained due to the combined influence of the following two factors: (i) the carboxymethyl groups increase the swellability of SA, thereby facilitating the diffusion of monomer (BA) and photo-initiator (CAN), and (ii) the ionization of carboxymethyl groups along the SA chains introduces the negative charges which attract ceric ions to the backbone leading to the formation of more active sites on the backbone which will be available to the monomer (BA), thereby increasing the reactivity of SA toward photo-grafting. Similarly, as investigated earlier by us, the higher values of grafting yields were also obtained in the case of photo-grafting of MA and MMA onto Na-PCMSA ($\overline{DS}$ = 1.10) in comparison with SA (Table 1).

Conclusions

In continuation of our earlier studies (Trivedi & Chourasia, 2024), we have compared the reactivity of BA with that of other acrylate monomers (MA and MMA) towards photo-grafting of them onto Na-PCMSA (DS = 1.10) using CAN as a photo-initiator. It has been observed that all

the acrylate monomers are not equally reactive towards photo-graft copolymerization. The plausible explanation has been furnished for the observed differences in the reactivity of acrylate monomers towards photo-grafting. It has been observed that BA is less reactive than MA and MMA towards photo-grafting. The effect of introducing the carboxymethyla group(s) in the SA molecules on its susceptibility towards photo-grafting of BA has been investigated and it has been observed that by changing the chemical structure of SA by carboxymethylation has enhanced its behavior towads photo-grafting of BA onto Na-PCMSA ($\overline{DS}$ = 1.10). The plausible explanation has been provided for this observation.

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