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N-tert-amylacrylamide based copolymers–I : Synthesis and Reactivity ratios of Poly(NTA-co-SY)

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Abstract: A series of copolymers N-tert-amylacrylamide (NTA) and Styrene(SY) were prepared by free radical polymerization in DMF at 60 ^{0}C using BPO as initiator. The copolymers were characterized by ^{1}H-NMR spectroscopy and the copolymer compositions were determined by ^{1}H-NMR analysis. The reactivity ratios of the monomers were determined by Fineman- Ross and Kelen-Tudos methods. The reactivity ratios of monomers determined by Fineman-Ross ($r_1 = 0.62$ and $r_2 = 3.52$), Kelen-Tudos ($r_1 = 0.62$ and $r_2 = 3.51$) . The $r_1.r_2$=2.18 indicates the formation of random copolymers. Mean Sequence lengths of copolymers are estimated from r_1 and r_2 values. It shows that the SY units increases in a linear fashion in the polymer chain as the concentration of SY increases in the monomer feed.

Keywords: N-tert-amylacrylamide, reactivity ratios, copolymer composition, Mean Sequence lengths.

Introduction

The chemical structure of a copolymer depends not only on the two-monomer units forming the macromolecule, but also on how such units are distributed along macromolecular chains. This distribution is a direct consequence of each monomer's reactivity in the copolymer molecule [1].

The N-substituted acrylamides are used to prepare thermo sensitive polymers like poly(N-isopropylacrylamide)and copolymers of N-alkyl acrylamide and styrene [2]. Thermosensitive polymers have great potential in applications as drug delivery system [3] human gene vector [4] and biocatalysts [5].

The determination of copolymer composition and reactivity ratios of the monomers is important in evaluating the specific application of the copolymer [6]. The monomer reactivity ratios determined by conventional linearization methods are not always accurate and several non-linear methods have been attempted to determine their value [7–9]. ^{1}H-NMR spectroscopic analysis has been established as a powerful tool for the estimation of copolymer composition [10, 11]. Knowledge of the copolymer composition is an important step in the evaluation of its utility. Copolymer composition and monomer distribution in the copolymer are dependent on the reactivity ratios. The most common mathematical model of copolymerization is based on finding the relationship between the composition of copolymers and the composition of the monomer feed in which the monomer reactivity ratios are the parameters to be determined [12]. The accurate estimation of copolymer composition and determination of monomer reactivity ratios are significant for tailor-made copolymers with required physical and chemical properties and in evaluating the specific end application of the copolymers.

The present article reports the synthesis and characterization of copolymers of N-tert-amylacrylamide with Styrene . The determination of monomer reactivity ratios of the monomers and mean sequence lengths of copolymers are also reported.

Experimental

Materials

Acrylonitrile was first washed with 5% NaOH solution in water to remove the inhibitor and then with 3% Orthophosphoric acid solution in water to remove basic impurities. Then the Acrylonitrile was washed with double distilled water and dried over anhydrous $CaCl_2$. The acrylonitrile was then distilled in an atmosphere of Nitrogen and reduced pressure. It was then collected in a clean dry amber coloured bottle and kept in the refrigerator at 5° C. Benzoyl proxide(BPO) was recrystallized from chloroform. N,N'-dimethylformamide(DMF) was dried in Megnesium Sulphate All the solvents were purified by distillation prior to their use. The comonomer styrene (SY) was purified by washing successively with 5% NaOH and distilled water, dried, and finally distilled at reduced pressure under nitrogen at 60 ^{0}C.

Preparation of N-tert-amylacrylamide (NTA)

The monomer N-tert-amylacrylamide was prepared by the reaction of t-amyl alcohol with acrylonitrile. N-tert-amylacrylamide was recrystallized in warm dry benzene. The white crystals have amp.91° C (Lit.91-92° C) and the yield was -87% [13].

^{1}H-NMR($CDCl_3$),δ(ppm) :

at 0.78ppm for-CH_3 , at 1.2ppm for-$(CH_3)_2$, at 1.7 ppm for- CH_2, at5.49 ppm for =CH vinylic proton and at 6.1ppm for vinylic =CH_2 proton

^{13}C-NMR($CDCl_3$),δ(ppm) :

δ 163.90(CH_2 = C(H)-$\underline{\text{CO}}$-NH..);
δ 132.93(CH_2 =$\underline{\text{C}}$(H)-CO-NH…);
δ 123.87($\underline{CH_2}$=C(H)-CO-NH..) ;
δ 52.82(-CO-NH-$\underline{\text{C}}$(CH_3)-CH_2);
δ 31.87(-CO-NH-C(CH_3)2-$\underline{CH_2}$-CH_3);
δ 26.19(-CO-NH-C($\underline{CH_3}$)2-CH_2-CH_3)
δ 8.26(-C$(CH_3)_2$-CH_2-$\underline{CH_3}$).

Copolymerization

A total feed of 5 gm of monomers N-tert-amylacrylamide , Styrene and 50mg of BPO initiator were dissolved in 25ml of DMF placed in a standard reaction tube to obtain a homogenous solution. The mixture was flushed with oxygen free dry nitrogen gas. The inlet and outlet of the reaction tube were closed by means of rubber tubing's and pinch cock. The reaction vessel is then immersed in a thermostatic water bath maintained at 60° C. The copolymerization reaction was allowed to proceed for an appropriate duration that would give a conversion below 10%. After the reaction vessel was removed from the thermostat and cooled under the tap. The solution poured in ice cold water to precipitate the copolymer and the copolymer washed with methanol. It was then dried in vacuum oven for 24 hours.

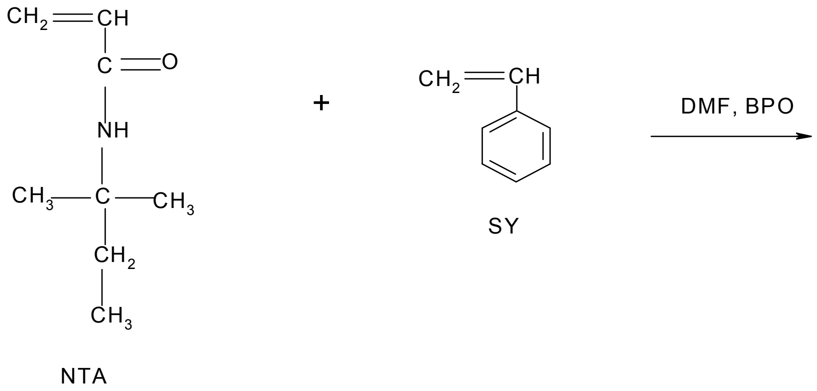
Instrumentation

The ^{1}H-NMR spectra of monomers and copolymers were recorded on the GSX-400 spectrometer(JEOL, Tokyo,Japan) operating at 400 MHz respectively in $CDCl_3$. A DSC - Q200 V23 , Differential scanning calorimeter was used to study the thermal behavior of copolymers at a heating rate of 20°C /min under nitrogen atmosphere. Thermogravimetric analysis was carried out using TGA Q500 V-20 at a heating rate of 20°C /min under nitrogen atmosphere.

Results and Discussion

Copolymerization

A series of copolymers N-tert-amylacrylamide (NTA) and Styrene(SY) were prepared by free radical polymerization in DMF at 60 ^{0}C using BPO as initiator. The schematic representation of the copolymer is given bellow:



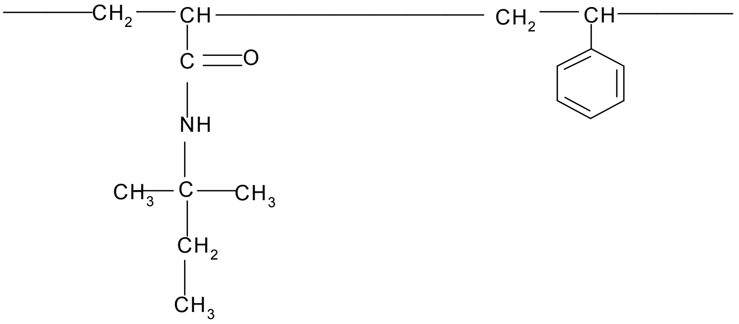


Figure 1: Copolymerization of N-tert-amylacrylamide and Styrene

Characterization

The ^{1}H-NMR spectrum of copolymer , poly (NTA-co- SY) (0.6 : 0.4) is shown in Figure 2. The following peaks appear in the copolymer spectrum : at 0.81 ppm for CH_3 (NTA) , at 1.25 ppm for tert –methyl group of NTA and 1.77ppm for -CH_2(NTA) , 2.3 ppm backbone CH_2 , at 2.53 ppm due to backbone methyne C-H , 6.62-7.42 ppm
for phenyl proton and at 8.05 ppm for N-H.

Determination of copolymer composition

The copolymer composition was determined ^{1}H-NMR spectral analysis of the copolymer. The assignment of the resonance peaks in the ^{1}H-NMR spectrum allows the accurate evaluation of the content of each kind of monomer incorporated into the copolymer chain.

The phenyl peak area**[11]** is used to determine the copolymer composition. Resonance signal at 6.62-7.42 ppm corresponds to aromatic proton and their integrated intensity of this peak is compared to the total intensities of all the peaks in the copolymer spectrum, which is a measure of their relative areas. The copolymer compositions can be obtained using

$$X_{SY} = \frac{15\ A\ (\text{phenyl})}{5A_{\text{total}} + 7A(\text{phenyl})} \quad (1)$$

Where X= mole fraction and A= peak area. Table 1. gives the values of the corresponding mole fractions in the copolymers.

Reactivity ratios

From the monomer feed ratios and the resultant copolymer compositions, the reactivity ratios of monomer 1 (NTA) and monomer 2 (SY) were evaluated by the methods of Fineman-Ross (F-R) and Kelen- Tudos (K-T). The significant parameters of F-R and K-T and equation are presented in Table 1 and Table 2 respectively. The reactivity ratios for NTA (r_1) and SY (r_2) from the F-R plot (Figure 3) and K-T plot are given in Table 3. The value(s) of r_1 is less than 1 and r_2 is greater than 1. The r_1 shows that NTA favors cross-propagation as opposed to homopropagation and r_2 shows that SY favors homopropagation over cross-propagation. The r_1 and r_2 together show that SY is generally reactive than NTA, hence the copolymers contain a higher proportion of SY units.

Mean sequence length

The mean sequence length was determined using the pertinent equations:

$$l_1 = r_1 \frac{M_1}{M_2} + 1 \quad \ldots\ldots..(2)$$

$$l_2 = r_2 \frac{M_2}{M_1} + 1 \quad \ldots\ldots.(3)$$

where r_1 and r_2 are the reactivity ratios and $[M_1]$and $[M_2]$ represent the concentration of NTA and SY respectively, in the monomer feed. The mean sequence lengths of copolymers are given in Table 4 . It is significant to note that from the Table 4, the SY units increases in a linear fashion in the polymer chain as the concentration of SY increases in the monomer feed.

Thermal analysis

The glass transition temperature (Tg) is the temperature at which the amorphous domain of a polymer takes on the characteristic properties of glassy state. The Tg depends on the morphology of the polymer and the Tg values are presented in Table 5 . The Tg of poly (N- tert-amylacrylamide) homopolymer is 86.2°C.The Tg of corresponding copolymers are increases with increasing feed content of SY. The increase in Tg may be attributed to a reduction in segmental mobility.

The TGA data for the ionomers of NTA with SY are given in Table 5 . A typical TGA curve for poly(NTA-co-SY) is shown in Figure 4. All the copolymers exhibit double stage decomposition. The initial decomposition temperature (IDT) increases with increasing feed of SY . Hence the stability of the copolymers increases with the increasing mol % SY. The maximum weight loss occurring in stage 2 may be due to scission in amide linkage and aryl ring of SY monomeric units of copolymer.

Table 1: Fineman-Ross parameters for the Copolymerization of N-tert-amylacrylamide and styrene

Mole fraction of NTA in feed,M_1	Mole fraction of SY in feed, M_2	Mole fraction of NTA in copolymer, m_1	Mole fraction of SY in copolymer, m_2	$F=M_1/M_2$	$F=m_1/m_2$	(f-1)/F	f/ F^2
0.2	0.8	0.06	0.94	0.250	0.064	- 3.744	1.024
0.3	0.7	0.12	0.88	0.429	0.136	-2.014	0.739
0.4	0.6	0.19	0.81	0.667	1.235	-1.147	0.528
0.5	0.5	0.24	0.76	1.000	0.315	-0.685	0.315
0.6	0.4	0.38	0.62	1.500	0.613	-0.258	0.272
0.7	0.3	0.49	0.51	2.333	0.961	-0.017	0.177
0.8	0.2	0.65	0.35	4.000	1.857	0.462	0.116

Table 2: kelen-Tudos parameters for the Copolymerization of N-tert-amylacrylamide and styrene

G =F(f-1) / f	H =F^2 / f	η =G /(α + H)	ε = H / (α + H)
-3.656	0.977	-0.943	0.252
-2.725	1.353	-0.641	0.318
-2.171	1.894	-0.453	0.395
-2.167	3.175	-0.357	0.523
-0.947	3.671	-0.144	0.559
-0.095	5.664	-0.011	0.661
1.846	8.616	0.160	0.748

α=2.90

Table 3. Copolymerization parameter, for the NTA and SY Copolymer.

Methods	r_1	r_2	$r_1 . r_2$
Fineman-Ross (F-R)	0.62	3.52	2.18
Kelen-Tudos (K-T)	0.62	3.51	2.14

Table 4. Mean Sequence Lengths in NTA and SY copolymerization[a]

SY in feed, M_2 (Mole %)	l_1	l_2	l_1 : l_2	Distribution [b]
0.80	1.16	15.08	1:15	N $(S)_{15}$N
0.70	1.26	9.20	1:9	N(S)$_9$ N
0.60	1.41	6.28	1:6	NSSSSSSN
0.50	1.62	4.52	2:5	NNSS SSSNN
0.40	1.93	3.35	2:3	
0.30	2.45	2.51	2:3	
0.20	3.48	1.88	3:2	

[a] r_1 = 0.62 , r_2 = 3.52

[b] Only a few cases are illustrated (N = NTA ; S=SY)

Table 5. TGA and DSC data for Poly(NTA-co-SY)

Copolymers	Mole fraction of NTA ,in feed	Mole fraction of SY, in feed	Mole fraction of SY,in copolymer	IDT (°C)	T_{50}(°C)	T_f (°C)	T_g (°C)
NTA-SY	0.60	0.40	0.62	156.23	415.52	452.92	74.22
NTA-SY	0.50	0.50	0.76	174.06	418.24	451.91	64.31
NTA-SY	0.40	0.60	0.81	233.39	423.29	453.08	70.63
Poly-NTA		-	-	-	-		86.2

IDT : Initial Decomposition Temperature
T_{50} : decomposition temperature at 50% weight loss
T_f : final decomposition temperature
T_g : glass transition temperature

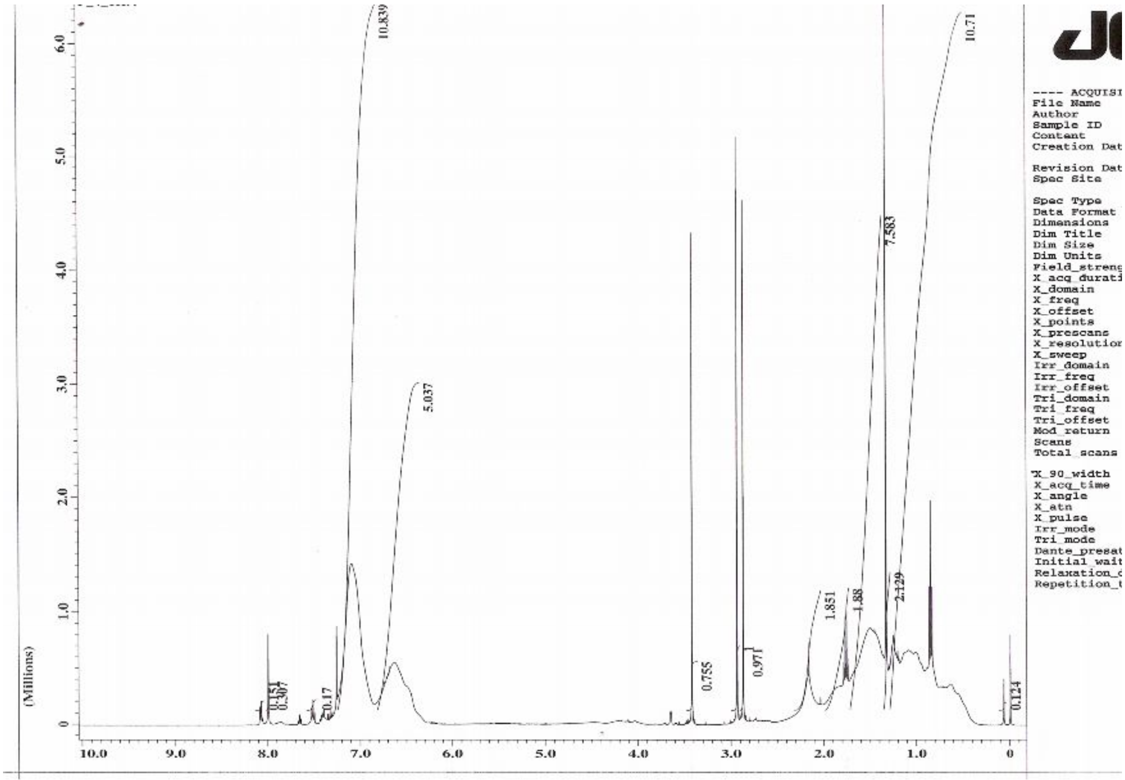


Figure 2: ^{1}H-NMR spectrum of poly (NTA-co- SY) (0.6 : 0.4)

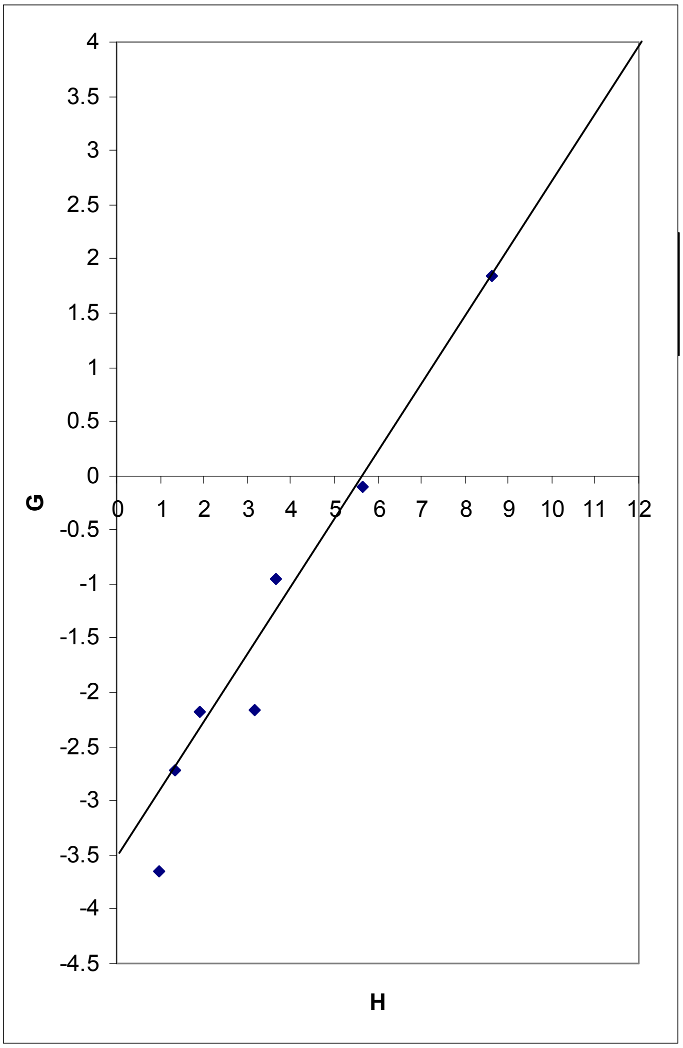


Figure 3 : Fineman-Ross (F-R) plot

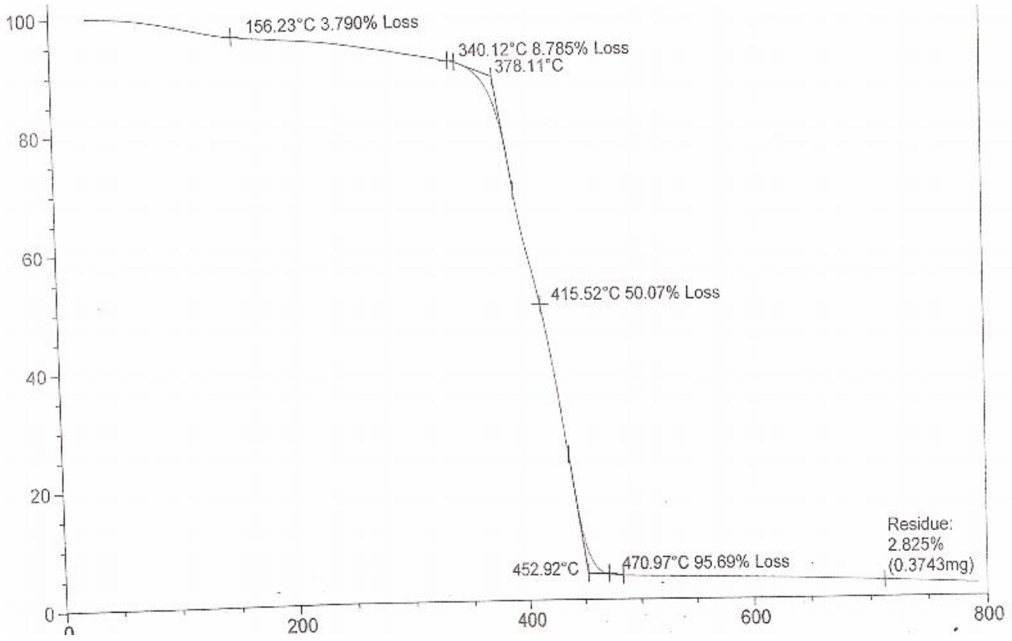


Figure 4 : TGA curve for poly(NTA-co-SY) (0.6 : 0. 4)

References

[1] Gatica N., Natali F., Alejandra O., Deodato R.: Synthesis and characterization of functionalized vinyl copolymers I: Structure-monomer reactivity relationship in copolymers containing N-vinyl-2-pyrrolidone moieties. Journal of the Chilean Chemical Society, **50**,581–585 (2005).

[2] Nichfor M., Zhu X. X.: Copolymers of N-alkylacrylamides and styrene as new thermosensitive materials. Polymer, **44**, 3053–3060 (2003).

[3] Leroux J., Roux E., Le Garrec D., Hong K., Drummond D. C.: N- isopropylacrylamide copolymers for the preparation of pH-sensitive liposomes and polymeric micelles. Journal of Controlled Release, **72**, 71–84 (2001).

[4] Kurisawa M., Yokayama M., Okano T.: Gene expression control by temperature with thermo-responsive polymeric gene carriers. Journal of Controlled Release, **69**, 127–137 (2000).

[5] Kofukuta E.: Novel application for stimulus-sensitive polymer gels in the preparation of functional immobilized biocatalysts. Advances in Polymer Science, **110**, 157–176 (1993).

[6] Pitchumani S., Rami Reddy B. S ., Rajadurai C.: Reactivity ratios of ethyl acrylate, n-butyl methacrylate copolymer system by ^{1}H-NMR analysis. Journal of Polymer Science: Polymer Chemistry Edition, **20**, 277–282 (1982).

[7] Dube M., Sanayei R. A., Penlidis A., O' Driscoll K. F., Reilly P. M.: A micro computer program for estimation of copolymerization reactivity ratios. Journal of Polymer Science, **29**, 703–708 (1991).

[8] Polic A. L., Duever T. A., Penlidis A.: Case studies and literature review on the estimation of copolymerization reactivity ratios. Journal of Polymer Science Part A: Polymer Chemistry, **36**, 813–822 (1998).

[9] Hagiopol C., Frangu O., Dumitru L.: A nonlinear method for estimation of reactivity ratios in copolymerization processes. Journal of Macromolecular Science Chemistry Edition, **26**, 1363–1379 (1989).

[10] Pazhanisamy P., Ariff M., Anwaruddin Q.: Copolymers of α- Methyl styrene with N-cyclohexylacrylamide: Synthesis, monomer reactivity ratios and mean sequence length. Journal of Macromolecular Science: Pure and Applied Chemistry, **34**, 1045–1054 (1997).

[11] Pazhanisamy P., Sulochana P., Anwaruddin Q., Ariff M.: Reactivity ratios of N-cyclohexylacrylamide and styrene copolymers by ^{1}H and ^{13}C- NMR spectroscopy. Journal of Polymer Science Part A: Polymer Chemistry, **35**, 193–195 (1997)

[12] Arshady R., Kenner, G. W., and Led with A. : Phenolic resins for solid-phase peptide synthesis: Copolymerization of styrene and p- acetoxystyrene, Journal of Polymer Science Polymer Chemistry Edition,**12 (9**), 2017 – 2025(1974)

[13] Pazhanisamy .P., and Reddy B. S. R. :Synthesis and characterization of methacrylamidopropyl trimethylammonium chloride and N- substituted acrylamide ionomers. eXPRESS Polymer Letters,1(11), 740–747 (2007).

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