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Synthesis of Poly [Allylamine-Co-Butadiene] form reduction of Poly [Acrylonitrile-Co-Butadiene] and grafting the product with Amic acids

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Abstract

Pure Poly [Allylamine-Co-Butadiene] having high molecular weight was prepared for the first time from the reduction of the Poly [Acrylonitrile-Co-Butadiene] using Lithium Aluminium hydride. Softening point of the prepared polymer was (201-207)°C, conversion percent was 88%, with intrinsic viscosity of the new polymer in benzene as a solvent was 1.56.

Then the new polymer was allowed to react with six acid anhydrides, (Maleic, Phthalic, Succinic, Glutaric, 1,8-Naphthalic and cis 1,2,3,4-tetrahydrophthalic) to produce six novel pendant polymers which contain the acids reffered above in its recurrent units. The prepared poly [N-(ally)substituted amic acid-Co-butadiene] polymers were characterized using FTIR, H-NMR, and some specific tests.

الخلاصة

حُضِرَ لاول مرة [اليل امين−مشترك−بيوتادايين] نقي ذو وزن جزيئي عالي من اختزال بولي [اكريلونايترايل−مشترك−بيوتادايين] باستخدام الليثيوم المنيوم هايدرايد وبدرجة تلين بين (207−201)°م ونسبة تحويل مئوية مقدارها 88%، اما اللزوجة الجوهرية للبوليمر الناتج في البنزين فكانت 1.56. تبع ذلك مفاعلة البوليمر الناتج مع ستة من انهيدريدات الحوامض (المالييئيك، الفثاليك، السكسنيك، الكلوتاريك، 8,1−نفثاليك وسيز 4,3,2,1−تتراهايدروفثاليك) مكونا بوليمرات جديدة، حاوية على الحوامض المذكورة اعلاه بشكل متدلي في وحداتها المتكررة. تم تشخيص جميع البوليمرات المحضرة باطياف FTIR ، H-NMR وبعض الكشوفات النوعية.

Introduction

Acrylonitrile-Co-butadiene rubber (NBR) is commonly considered the workhorse of the industrial and auto-motive rubber products industries. NBR is actually a complex family of unsaturated copolymers of acrylonitrile and butadiene. By selecting an elastomer with the appropriate arcylo-nitrile content in balance with other properties, the rubber compounder can use NBR in a wide variety of appl-ication areas requiring oil, fuel, and chemical resistance, with a temperature range of -40°C to +125°C. NBR mater-ials can withstand all but the most severe automotive applications(1).

NBR is produced in an emulsion polymerization system(2). NBR prod-ucers vary polymerization tempera-tures to make "hot" and "cold" polymers. Specially NBR polymers which contain a third monomer (e.g. divinyl benzene, methacrylic acid) are also offered.

The Acrylonitrile (CAN) content is one of two primary criteria defining each specific NBR grade(3,4).

Cold polymers are polymerized at a temperature range of (5-15)°C, depending on the balance of linear-to-branched configuration desired. The lower polymerization temperatures yield more-linear polymer chains(5).

Hot NBR polymers are polymerized at the temperature range of (30-40)°C. this process yields highly branched polymers. Branching supp-orts good tack and a strong bond in adhesive applications(5).

Addition of carbolxylic acid groups to the NBR polymers backbone significantly alters processing and cured properties(6).

Copolymeriztion of allylamine with butadiene is difficult to achieve by emulsion polymerization method due to the stability of the allylic radicals or ions(7), therefore initially formed active centers are not reactive enough to propergate and form high molecular weight chains.

Experimental

Reduction of poly [Acrylonitrile-Co-Butadiene] (NBR)

Literature procedures were used with some modifications(8-9). A solution of 3g (0.03 mole) lithium aluminum hydride in 60 ml of dry tetrahydrofurane (THF) was placed in a 500 ml two necked flask provided with a magnetic bar, reflux condenser attached to a calcium chloride tube, and 250 ml dropping funnel. 1.2 gm (0.03 mole) of poly[Acrylonitrile-Co-Butadiene] dissolved in 70 ml of THF was placed in dropping funnel. The poly[Acrylonitrile-Co-Butadiene] solution was added dropwise to the flask with stirring for 30 minutes, after which the mixture was refluxed gently for overnight. Excess of water was added in order to decompose the unreacted lithium aluminum hydride.

The mixture was acidified with dilute hydrochloric acid to remove Aluminum hydroxide then stirred for ten minutes. The mixture was transferred to a separatory funnel. The THF layer was separated and treated with dilute sodium hydroxide solution. When a viscous precipitate was formed, it was purified by dissolving in benzene and reprecipitated in petroleum ether. The yield was 2.64g (88%). The softening point of the polymer was (201-207)°C, intrinsic viscosity was 1.56, an the colour was gray.

Preparation of Poly [N-(allyl) substituted amic acid-Co-Butadiene]

Literature procedures were followed in the preparation with minor modifications(10-11). In 250 ml round bottom flask with magnetic bar fitted with dropping funnel and reflux condenser, was placed (0.02 mole) of either the anhydrides of (Maliec, Phthalic, Succinic, Glutaric, 1,8-Naphthalic, and cis 1,2,3,4-tetrahydro-phathalic), plus 50 ml of suitable solvent such as benzene, dioxane or chloroform.

When all the anhydrides were dissolved by stirring, a solution of (0.02 mole) of the prepared poly [Allylamine -Co- Butadiene] in 80 ml of benzene or dioxane was allowed to run through the dropping funnel dropwise. The addition was performed dropwise with stirring for half an hour. Then the mixture was refluxed on a water bath at temperatures (80-100)°C, stirring was continued for further (6-8) hrs. The poly[N-(allyl)amic acid-Co-butadiene] did not precipitate. The solution was evaporated under reduced pressure. Then polymeric product was purified by dissolving in sodium bicarbonate solution (10%) and reprecipitated in dilute hydrochloric acid. The precipitate was washed with cold water and dried. The physical properties of the resulting poly [amic acid] are listed in tables (I-III).

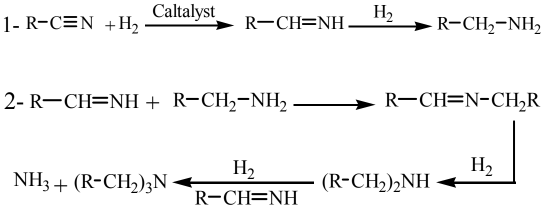
Result and Discussion

Nitrile group is reduced to primary amine group by two ways(12):

1- Catalytic hydrogenation.

2- Lithium Aluminum hydride.

In the first method the reduction caused the formation of a mixture of tertiary, secondary and primary amines according to the following equations:



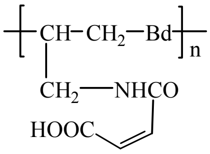
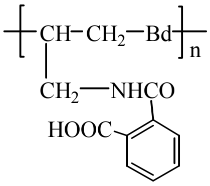
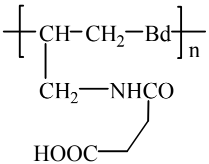
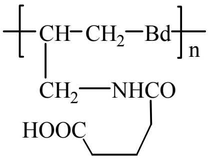
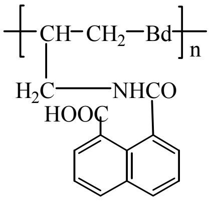
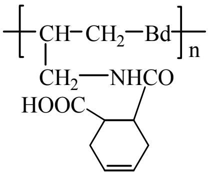
$$1\text{- } R{-}C{\equiv}N + H_2 \xrightarrow{\text{Caltalyst}} R{-}CH{=}NH \xrightarrow{H_2} R{-}CH_2{-}NH_2$$

$$2\text{- } R{-}CH{=}NH + R{-}CH_2{-}NH_2 \longrightarrow R{-}CH{=}N{-}CH_2R \xrightarrow{H_2} (R{-}CH_2)_2NH \xrightarrow[R{-}CH{=}NH]{H_2} NH_3 + (R{-}CH_2)_3N$$

R= alkyl or phenyl

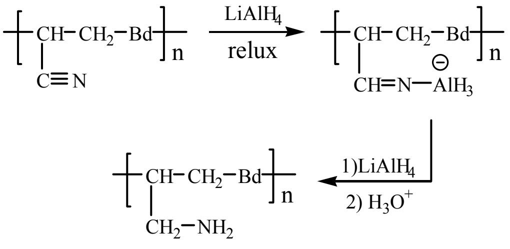
Also the use of H_2/Catalyst caused the reduction of double bond in the polymer, so it was used excess of $LiAlH_4$ to reduce the conversion of poly[Acrylonitril-Co-Butadiene] to poly[Allylamine-Co-Butadiene] in dry refluxing THF according to the literature.

Table (I): physical properties of the prepared polymers having pendant amic acid

Compound	%conversion	Softening points (°C)	Colour	Intrinsic Viscostity
	87	231-238	White-gray	1.57
	80	215-219	White-gray	1.65
	78	186-192	White	1.58
	81	185-191	White	1.59
	68	275d	Yellow	1.73
	78	240-250	White-yellow	1.61

Bd= $-CH_2-CH=CH-CH_2-$

The mechanism of the reduction includes the formation of an intermediate imino salt followed by hydrolysis.



Bd = $-CH_2-CH=CH-CH_2-$

The product poly [Allylamine-Co-Butadiene] was obtained in a high conversion and high molecular weight.

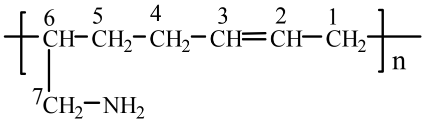
The reaction should be carried out in dry conditions as the existence of water caused the water to react with $LiAlH_4$ according to the following equations[13].

$$LiAlH_4 + 4H_2O \text{ (excess)} \longrightarrow LiOH + Al(OH)_3 + 4H_2$$

$$LiAlH_4 + 2H_2O \text{ (excess)} \longrightarrow LiAlO_2 + 4H_2$$

The prepared polymer is also soluble in hot THF or benzene, but sparingly soluble in water. FTIR spectra of the prepared poly [Allyl-amine-Co-Butadiene] show strong absorptions for ν-NH_2 group at (3320-3435)cm^{-1}; νC=C olefins at 1630 cm^{-1}, δN-H bending (1580-1595) cm^{-1}, and ν-CH$_2$ at 2900 cm^{-1}.

The H-NMR spectrum in benzene-d6 showed the following chemical shifts:



$$\left[\overset{6}{CH}(\overset{7}{CH_2}-NH_2)-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_2}\right]_n$$

δ1.6 (q, 2H) for $-\overset{5}{CH_2}-$

δ1.9 (t, 2H) for $-\overset{1}{CH_2}]_n$

δ2.1 (q, 2H) for $-\overset{4}{CH_2}-$

δ2.6 (m, 1H) for $[\overset{6}{CH_2}-$

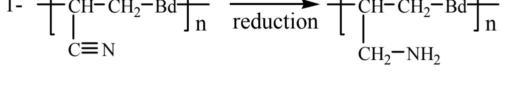
δ4.2 (q, 2H) for $-\overset{7}{CH_2}-$

δ5.43 (m, 2H) for $-\overset{2}{CH}=\overset{3}{CH}-$

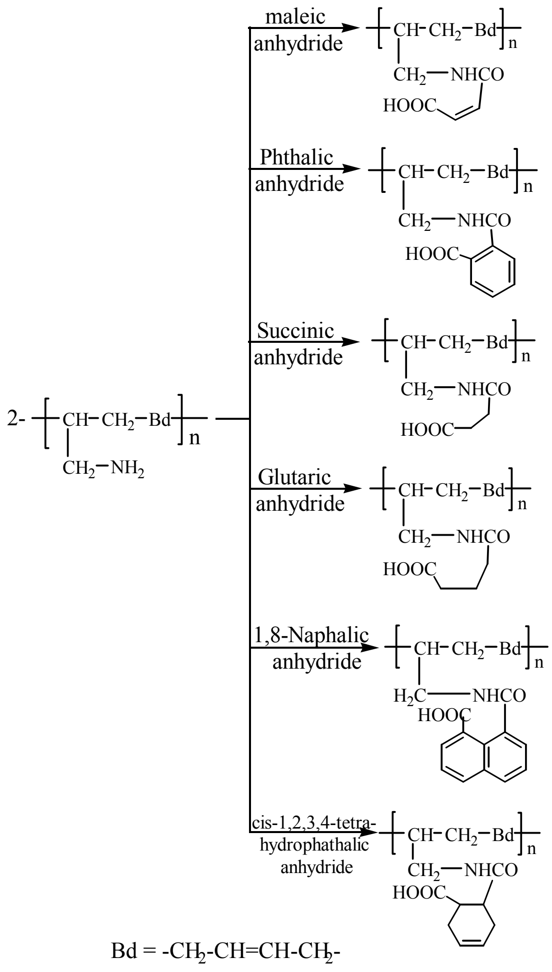
δ8.7 (s, 2H) for $-NH_2$

Rimini test which was specific for primary aliphatic amine was carried out to characterize the prepared polymers$^{(14)}$.

Six novel polymers were derived from the prepared poly [N(allylamine)-Co-butadiene] namely, which include poly [N(allylmalemic acid)-Co-Butadiene], (phthalamic acid, succinamic acid, glutaramic acid, 1,8-nephthalamic acid, and cis 1,2,3,4-tetrahydrophthalamic acid). The new polymers were prepared by allowing a benzene or dioxin solutions of poly [allylamine-Co-butadiene]to react with corresponding anhydrides following literature procedures. Table (I) lists softening points percent conversion, colour, and intrinsic viscosities of prepared polymers having pendant amic acids. Scheme I shows the performed reactions and transfor-mations.



$$1-\ \left[CH(C\equiv N)-CH_2-Bd\right]_n \xrightarrow[\text{reduction}]{LiAlH_4} \left[CH(CH_2-NH_2)-CH_2-Bd\right]_n$$



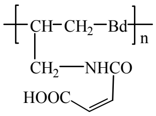
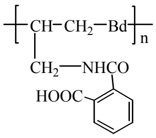
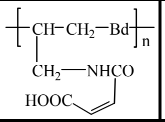
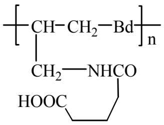
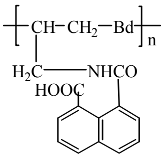
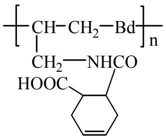
Bd = -CH$_2$-CH=CH-CH$_2$-

Scheme -I-

The poly [N-(allyl) substituted amic acid-Co-butadiene] are characterized by their FTIR spectra which are listed in table II and the chemical reaction with NaHCO$_3$ solution mentioned earlier. FTIR spectra of the products showed medium intensity band at (3350-3290) cm^{-1} for NH stretching. The –COOH absorption was found at (3250-2700) cm^{-1}. However, it overlaps with (C-H) aliphatic stretching absorption. Two bands related to ν$_{C=O}$ were observed at (1720-1700) and (1640-1625) cm^{-1} for both Carboxylic acid and amide groups respectively.

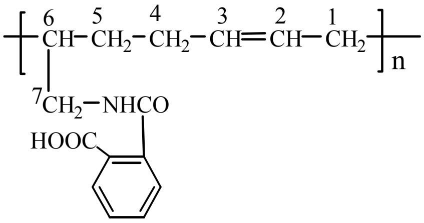
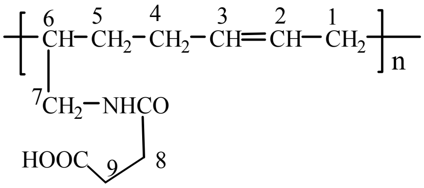
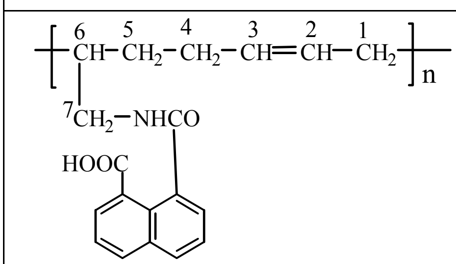
The H-NMR spectrum of some prepared amic acid are listed in table III in DMSO-d6 solvent.

Table (II): FTIR absorpation (cm^{-1}) of the prepared polymers having pendant amic acid

Compound	Major FTIR (cm^{-1})			
	νN-H	νC=O carboxylic	νC=O amid	νC=C aliphathic
	3310	1710	1635	1610
	3290	1700	1640	1620
	3350	1720	1630	1610
	3340	1720	1635	1620
	3295	1700	1640	1625
	3300	1710	1625	1610

Bd= $-CH_2-CH=CH-CH_2-$

Table (III): ^{1}H-NMR of the some poly [N(allyl-Co-butadiene) substituted amic acids] in DMSO-d^6

Compound	^{1}H-NMR spectral data (δ)
	1.9(d, 2H, -$\overset{1}{C}H_2$) ; 5.42(q, 2H, -$\overset{3}{C}H$=$\overset{2}{C}H$-); 2.3(q, 2H, -$\overset{4}{C}H_2$-); 1.7(q, 2H, -$\overset{5}{C}H_2$-); 2.7(m, 1H, -$\overset{6}{C}H$-); 2.9(t, 2H, -$\overset{7}{C}H_2$-); 7.86(s, 1H, -NHCO-); 7.6(m, 4H, aromatic Protons); 12.2 (brod, 1H, carboxylic proton)
	1.9(d, 2H, -$\overset{1}{C}H_2$) ; 5.42(q, 2H, -$\overset{3}{C}H$=$\overset{2}{C}H$-); 2.3(q, 2H, -$\overset{4}{C}H_2$-); 1.7(q, 2H, -$\overset{5}{C}H_2$-); 2.7(m, 1H, -$\overset{6}{C}H$-); 2.9(d, 2H, -$\overset{7}{C}H_2$-); 7.2(s, 1H, -NHCO-); 2.3(t, 2H, CO-$\overset{8}{C}H_2$-); 2.6(t,2H,-$\overset{9}{C}H_2$-); 11.4(s,1H, carboxylic proton)
	1.9(d, 2H, -$\overset{1}{C}H_2$) ; 5.42(q, 2H, -$\overset{3}{C}H$=$\overset{2}{C}H$-); 2.3(q, 2H, -$\overset{4}{C}H_2$-); 1.7(q, 2H, -$\overset{5}{C}H_2$-); 2.7(m, 1H, -$\overset{6}{C}H$-); 2.9(d, 2H, -$\overset{7}{C}H_2$-); 7.2(s, 1H, -NHCO-); 7.8(m, $_6$H, aromatic proton); 12.3 (s, $_1$H, carboxylic proton)

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