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Acrylonitrile block copolymers

1. Preparation of polyacrylonitrile containing azo-linkage in the main chain by anionic insertion polymerization

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SUMMARY

Acrylonitrile was polymerized by an insertion process on being added to solutions containing the adduct of the reaction of tetrakis(dimethylamino) titanium (T4) and azobisisobutyronitrile (AIBN) .The obtained azo-linked polyacrylonitrile has appropriate initiating functionality for a subsequent vinyl polymerization.

INTRODUCTION

In recent years, there has been growing interest in the synthesis of novel materials with specific properties.Block copolymers which provide a combination of the physical properties are the most suitable materials for various purposes.The synthesis, characterization and properties of block copolymers have recently been reviewed by several authors[1-3]. Transformation reactions extend the range of possible monomer combinations in block copolymers[3].These methods generally involve a two-step procedure in which thermo or photolabile polymer is prepared by one mode and then precipitated, isolated and purified.Subsequently, these prepolymers are used to initiate the polymerization of a second monomer.Polymers containing an azo-linkage in the main chain are especiallly suitable for this purpose and can be prepared by means of condensation[4-5] and cationic[6-7] and anionic[8] living polymerization techniques.

Block copolymers with polyacrylonitrile and polymethacrylonitrile as one component are of potential interest in the development of high-tech devices such as lithography due to their polarity,solubility and high plasma etching resistance properties[9].Conventional anionic techniuqes are not suitable, especially when acrylonitrile is used as the first component, due to reactions at the C=N as well as the C=C bonds leading to insoluble crosslinked polymers. Jenkins and co-workers[10-12] have described a

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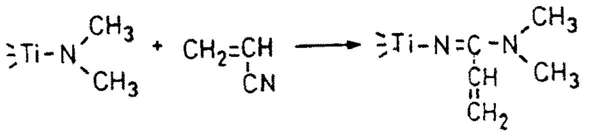
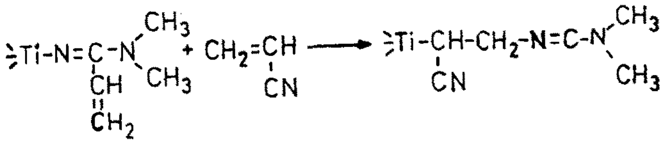
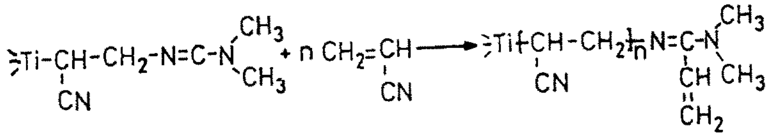
new system for the polymerization of monomers containing CN groups.Polymerization proceeds smoothly when related monomer is mixed with tetrakis(dimethylamino)titanium (T_4) according to following reactions.



$$>Ti-N(CH_3)_2 + CH_2{=}CH(CN) \longrightarrow >Ti-N{=}C(CH{=}CH_2)-N(CH_3)_2 \qquad (1)$$



$$>Ti-N{=}C(CH{=}CH_2)-N(CH_3)_2 + CH_2{=}CH(CN) \longrightarrow >Ti-CH(CN)-CH_2-N{=}C-N(CH_3)_2 \qquad (2)$$



$$>Ti-CH(CN)-CH_2-N{=}C-N(CH_3)_2 + n\,CH_2{=}CH(CN) \longrightarrow >Ti\!\left[CH(CN)-CH_2\right]_n N{=}C(CH{=}CH_2)-N(CH_3)_2 \qquad (3)$$

It seemed appropriate to use the same reaction principle between CN groups of the well known free radical initiator azobisisobutyronitrile (AIBN) and T_4 to initiate the polymerization of acrylonitrile.This procedure makes it possible to synthesize polyacrylonitrile containing an azo-linkage in the main chain.

EXPERIMENTAL

Materials:

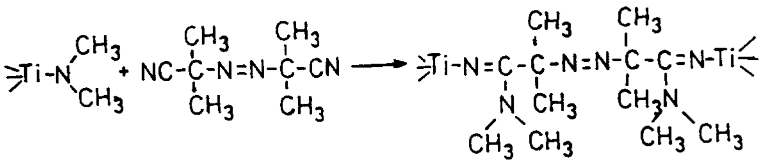
Tetrakis(dimethylamino)titanium (T_4) (Alfa/Ventron) was used without further purification.Benzene was washed succesively with H_2SO_4, water and alkali and distilled over $CaCl_2$ and refluxed over Na wire for 4 hours under nitrogen and finally distilled before use.Acrylonitrile (AN) was washed succesively with aqueous NaOH and water and distilled over CaH_2.

Polymerization Procedures:

The appropriate amount of T_4 was dissolved in benzene under nitrogen to give 12 % (w/w) solution.A Stoichiometric amount of AIBN was allowed to react with T_4 solution under nitrogen at 30°C for 96 hours.At the end of this period, the colour of the solution is darkened indicating completion of the reaction.A given amount of the above solution was immediately added to the monomer, previously dissolved in the same solvent, at 18-23°C.The reaction was allowed to proceed for 40 minutes with continious stirring.The polymers were then precipitated into methanol, dried and weighed.

RESULTS AND DISCUSSION

T_4 was permitted to react with AIBN under anhydrous conditions at ambient temperatures according to the following reaction.In this case, a coordination type of reaction between T_4 and the low molar mass initiator AIBN is operative.



$$>Ti-N\begin{matrix}CH_3\\CH_3\end{matrix} + NC-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-CN \longrightarrow >Ti-N=\underset{N(CH_3)_2}{C}-\underset{CH_3}{\overset{CH_3}{C}}-N=N-\underset{CH_3}{\overset{CH_3}{C}}-\underset{N(CH_3)_2}{C}=N-Ti<$$

(4)

The organometallic initiator was characterized by infrared spectra in benzene.As shown in Figure 1, strong absorption appears at 1600 cm^{-1} indicating $-N=C<$ groups, whereas weak nitrile absorbtion at 2220 cm^{-1} indicates the presence of a small amount of unreacted C≡N groups.Obviously, this would result in homopolymer formation in the subsequent block copolymerization step.One way to overcome this problem is to use excess T_4, which requires to be removed from the mixture at the end of the reaction since T_4 itself produces effective initiating specieces in the polymerization of AN according to reactions 1-3.Further studies are progress at this point.Polymerization of AN was carried out using the adduct as initiator.The results are shown in Table 1.

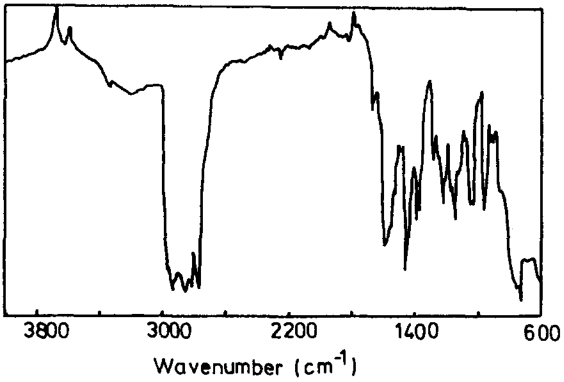
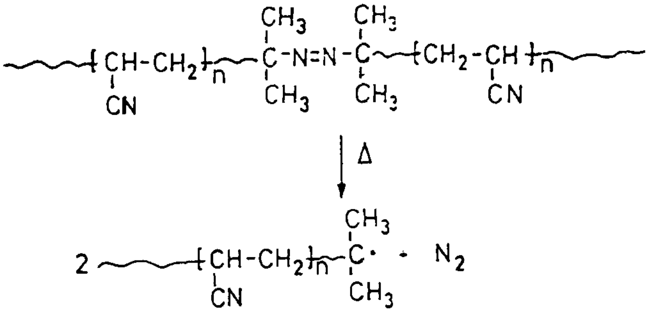


Figure 1: Infrared spectra of the adduct in benzene

Table 1.
Polymerization of actylonitrile initiated by the adduct in benzene.

Run No	AN (mol l^{-1})	The adduct (mol l^{-1})	Temp. (°C)	Time (min.)	Conversion (%)
1	3.02	1.3×10^{-4}	18-23	40	0.1
2	3.02	2.6×10^{-4}	18-23	40	15.5
3	0.75	5.3×10^{-4}	18-23	40	14
4	2.26	5.3×10^{-4}	18-23	40	46
5	3.77	5.3×10^{-4}	18-23	40	68

The polymerization of AN initiated by the preformed adduct is a very efficient process and at high concentrations of the monomer vigorous polymerization was observed with in a few seconds.Similarly, the adduct initiator obtained from the low molar mass model compound propionitrile produced initiation efficiency comparable to that of T_4 as was shown by Billingham et al.[11].This process leads to a polymer with -N=N- groups in the main chain. Polyacrylonitrile (PAN) functionalized in this way will decompose on heating and forms two radicals in a similar way to AIBN.



$$\sim\left[\underset{\mathrm{CN}}{\mathrm{CH}}-\mathrm{CH_2}\right]_n\sim\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}-\mathrm{N{=}N}-\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\sim\left[\mathrm{CH_2}-\underset{\mathrm{CN}}{\mathrm{CH}}\right]_n\sim$$

$$\Big\downarrow \Delta$$

$$2\sim\left[\underset{\mathrm{CN}}{\mathrm{CH}}-\mathrm{CH_2}\right]_n\sim\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C}}}\cdot + \mathrm{N_2}$$

(5)

If the thermolysis is carried out in the presence of free radically polymerizable monomers such as styrene (St) and methyl methacrylate (MMA), the polyacrylonitrile attached radical may initiate free radical polymerization to generate copolymers.As a crude demonstration, PAN (obtained from run 5) was used to the initiate the polymerization of St.A solution of St in DMF (1/1;v/v) containing 14.6 g/l PAN was heated at 65°C for 90 minutes.The resulting polymer was presumed to contain a copolymer of poly(AN-St) with 7.92 % overall St conversion and was soluble in benzene and THF which are non-solvent for homopolyacrylonitrile.A control experiment, in the absence of the initiator gave about 0.5 % conversion of St after 90 minutes heating at the same temperature.Efficiency of azo-linked PAN as a free radical initiator is not optimized in any way since each polymer chain contains one functionality and can produce only two polymeric radicals.The type of the block copolymer greatly depends on the kinetic behaviour of the particular monomer involved.Initiation of St polymerization by means of azo-linked PAN is expected to yield PSt molecules with PAN unit at each end since termination is by radical-radical combination.

Although these results preliminary in nature, they clearly indicate a useful two-step polymerization process by means of which copolymers of AN with different monomers can ultimately be generated by use of T_4. Detailed studies on the block copolymerization are now in progress and the results will be reported elsewhere.

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