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Free radical grafting onto cellulose in homogeneous conditions
1. Modified cellulose–acrylonitrile system

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Abstract

Synthesis of cellulose–polyacrylonitrile copolymers has been studied in a homogeneous solution of *N,N*-dimethylacetamide/LiCl. The method is based on the preliminary reaction of a portion of OH cellulosic groups with acryloyl chloride to give cellulose with a certain number of pendant double bonds. Successively, acrylonitrile is grafted onto the unsaturated groups by free radical polymerization using azobisisobutyronitrile as initiator. The optimum grafting conditions are evaluated by changing reaction temperature, as well as monomer/initiator and monomer/unsaturated group molar ratios. The products are characterized by size exclusion chromatography, i.r. and ^{13}C n.m.r. spectroscopy and a possible reaction mechanism is deduced. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: Cellulose copolymers; Radical grafting; Polyacrylonitrile

1. Introduction

Cellulose graft copolymers is the general name given to a class of cellulose derivatives containing polymeric side chains, covalently linked to an oxygen of the glucosidic unit. Since 1950, different olefines have been grafted onto cellulose and starch (Hebeish and Guthrie, 1981) with the aim of preparing new products having peculiar properties. Grafting processes used nowadays typically proceed under heterogeneous conditions: cellulose in the solid state is attacked by a number of chemical agents in order to undergo free-radical or ionic grafting, the free-radical methods being the most common ones. Aqueous solutions of peroxides, persulfates and redox systems (e.g. Ce^{4+} or Fe^{2+}/H_2O_2) can be used in the initiation step: however, depending on the olefin chemical nature, other suitable solvents, such as acetic acid, dimethylsulfoxide, sulfuric acid or mixed polar solvents, may replace water. The final product, after separation from the reaction medium, is always a mixture of graft copolymer, unreacted cellulose and olefin homopolymer, the proportion among the three components depending on the processing conditions.

While polyolefin extraction by a selective solvent does not present any difficulty, separation of the unreacted cellulose from the copolymer has never been successfully achieved. As a consequence, there is a lack of knowledge about the neat copolymer behaviour, with particular regard to the influence of number and length of side branches on its properties.

The discovery of new solvents of cellulose (Maia et al., 1981) in the last decades opened the possibility of performing derivatization and/or grafting reactions in homogeneous conditions, thus assuring important advantages, such as a better control of the substitution degree, a more uniform distribution of substituents along the polymer chain and a higher conversion yield.

Although a number of cellulose derivatives has already been synthesized under homogeneous conditions, for instance by using a dimethylsulfoxide (DMSO)–paraformaldeyde pair as the solvent for cellulose (Nishioka and Kosai, 1981; Nishioka et al., 1983), grafting reactions are still performed nowadays essentially on heterogeneous systems. The main disadvantage consists in both the production of non-homogeneous products and in poor reproducibility of the syntheses (Diamantoglou and Kundinger, 1995). In the present paper we report the results concerning the grafting of polyacrylonitrile (PAN) chains onto cellulose (CE), partially derivatized by an unsaturated acyl chloride, all the above steps occurring in the homogeneous phase. Conditions to obtain a predetermined percent of grafted polyolefin are also indicated.

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2. Experimental

2.1. Materials

Two samples of regenerated CE having DP 250 and 490 (CE1 and CE2, respectively) were supplied by 'Stazione Sperimentale Cellulosa, Carta e Fibre Tessili Vegetali ed Artificiali' (Milan, Italy). Before use, the samples were submitted to double extraction with water and petroleum ether, followed by oven drying at 50°C for 7 days under vacuum. A stock solution of CE in *N*,*N*-dimethylacetamide (DMAc)/5% LiCl at the polymer concentration (c_p) ~4% (w/w) has been prepared according to Turback's procedure (Turback et al., 1981).

DMAc was supplied by Fluka. It was dried by vacuum distillation on CaH_2 and stored on molecular sieves (Riedel-de-Haen type 4A), under nitrogen atmosphere.

LiCl (Fluka) was dried at 200°C for 24 h.

Acryloyl chloride (ACOCl), α,α'-azobisisobutyronitrile (AIBN), *N*,*N*-dimethylformamide (DMF), methanol, acetone (Fluka) were used as received.

Acrylonitrile (AN), supplied by Merck, was first washed with 10% NaOH to extract the polymerization inhibitor (hydroquinone), then washed with deionized water to neutral pH, and finally dehydrated over anhydrous Na_2SO_4.

2.2. Derivatization and grafting procedures

The cellulose–acrylonitrile copolymer (CEPAN) was synthesized following the two steps below: (a) synthesis of cellulose acrylate (CE-A); (b) grafting of AN on CE-A.

(a) The first step involves the dilution of CE stock solution with DMAc to $c_p = 2.5\%$, under anhydrous N_2. After cooling to 0°C, a suitable amount of ACOCl was added to the reaction medium and the derivatization reaction developed under mild stirring. After 3 h the unreacted ACOCl and the HCl produced during the acylation reaction were stripped out by N_2 flow up to neutral reaction of the gas. A suitable aliquot of solution was used to determine the degree of substitution, DS (DS being the number of –OH groups reacted with ACOCl per cellulose repeat unit, varying from 0 to 3) (Doelker, 1993). DS was determined by weight increase of the derivatized polymer with respect to its initial value (see below).

(b) The second aliquot of CE-A was diluted with DMAc to $c_p = 1\%$ and, consequently, c_{LiCl} decreased to 1.25%. Despite the rather low content of LiCl, no precipitate of CE-A was observed even at low DS. After increasing T to the reaction temperature, suitable amounts of AN and AIBN dissolved in a few milliliters of DMAc were added to the polymer solution, and the mixture left to react under stirring for 6 h. Addition of water caused the formation of a precipitate, consisting of both the CEPAN copolymer and the PAN homopolymer synthesized during the grafting step. After filtration, followed by washing (firstly with water, then with methanol) and drying under vacuum at 50°C, the precipitate was treated with DMF, a good solvent of PAN homopolymer, under reflux conditions for 2 h. The residue (neat CEPAN) was weighed: from the increase of its weight with respect of both CE and CE-A, the amount of grafted PAN was calculated.

2.3. Characterization methods

2.3.1. SEC

A Waters Chromatograph model 950 A1, equipped with three columns of 25 cm × 6 mm, having separation limits of 10 000, 1000, and 500 Å, respectively, was used to analyse the products after the grafting process. Solvent flux was settled at 1 ml min^{-1}.

2.3.2. I.r. spectra

Infrared spectra were obtained by using a FT-i.r. Bruker IFS model 66.

2.3.3. N.m.r.

A Bruker 500 spectrofotometer was employed. Spectra interpretation was performed on the basis of the software program SpecInfo 3.1.6.

3. Results and discussion

As mentioned in Section 2, DS values can be evaluated from the weight increase referred to the underivatized CE, according to the relationship:

$$DS = (W_{CE-A} - W_{CE})/(55 - 1)n_{CE}$$

where W_{CE} and $W_{CE\text{-}A}$ are the weights of the sample before and after derivatization, respectively; n_{CE} the moles of repeat (glucosidic) units in W_{CE} and 55 the molecular weight of the substituent.

In principle, DS could be alternatively obtained by back-titration of the unreacted acyl chloride, as already discussed in our previous paper related to the synthesis of cellulose propionate (Bianchi et al., 1997). However, the latter method requires the precipitation of the cellulose derivative by water, and the simultaneous hydrolysis of the unreacted acyl chloride which, after filtration, may be titrated as HCl. Unfortunately, in the present case, the water precipitate of cellulose-containing acrylate groups is rather difficult to filter, so that titration has been abandoned and all DS values of our CE-A samples have been obtained by the weight increase method only.

Table 1
Substitution degree (DS) at different ACOCl/glucosidic unit ratios

Sample	ACOCL/glucosidic unit (mol/mol)	DS
1	3	0.77
2	2	0.42
3	1.5	0.30

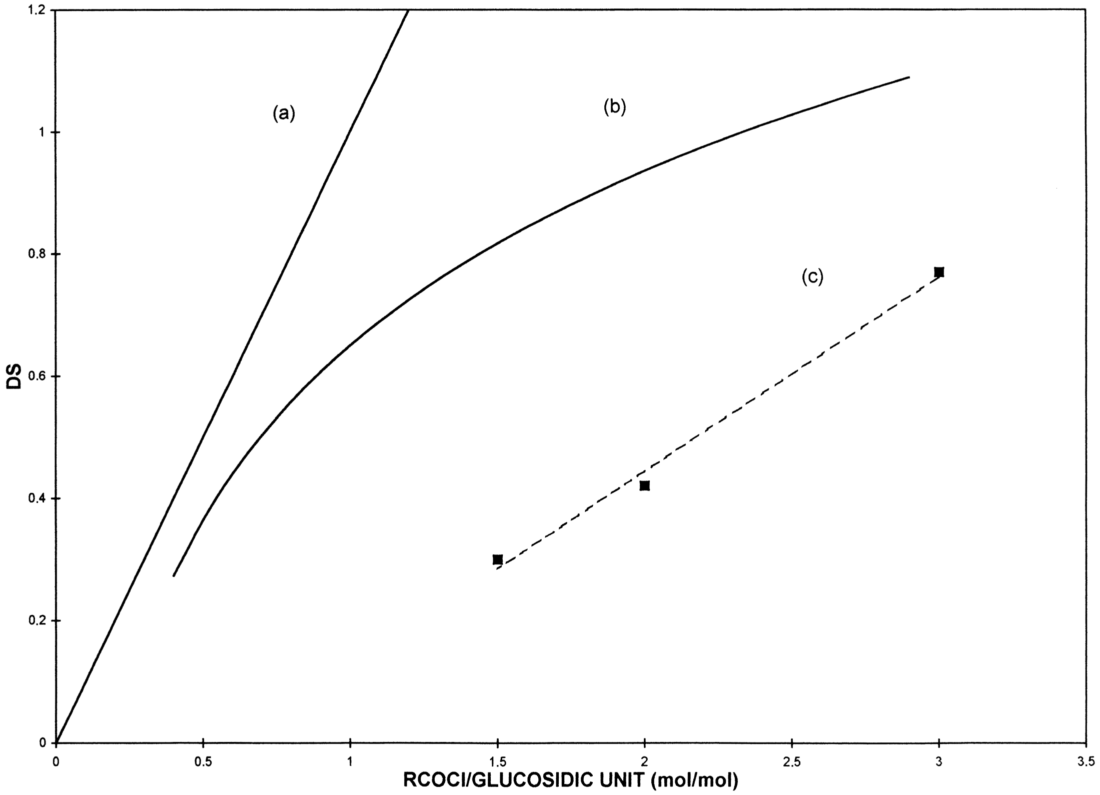


Fig. 1. Substitution degree of derivatized cellulose versus the molar ratio RCOCl/glucosidic unit.

The first set of experimental data has the scope to correlate DS values to the molar ratios between ACOCl and glucosidic repeat units. The results are collected in Table 1 and shown in Fig. 1, where they (curve *c*) are compared to the corresponding ones (curve *b*), previously found for propionyl chloride (see above). From the two curves it is evident that, as expected, acryloyl chloride is far less reactive than propionyl chloride, due to the presence of the double bond conjugated to the carbonyl group.

Curve *a* in Fig. 1 gives the maximum (theoretical) yield with respect to ACOCl, corresponding to its complete reaction with all –OH functions of the glucosidic ring.

Specific conditions to obtain higher DS values have not been purposely explored, in order to avoid rather large amounts of grafted PAN. In fact, the amount of PAN grafted in step (b) is directly linked to the extent of DS, and too high values of the latter would produce grafting yields exceeding the optimum value for several applications. For instance, with DS = 0.3 and a PAN chain (grafted to the –OH group) formed by five repeat units on average, the w/w percent of grafted polymer is already about 30%. Higher values are completely undesirable. Therefore, the conditions chosen for the reaction between CE and ACOCl are those which give DS~0.3.

Table 2
Characterization data of CEPAN samples

Sample	DS	AN/-A (mol/mol)	AN/AIBN (mol/mol)	T_{reaction} (°C)	$GP_1\%$[a]	$GP_2\%$[b]
CEPAN 1	0.33	10	50	60	17	5
CEPAN 2	0.27	25	50	60	47	35
CEPAN 3	0.32	25	30	60	65	49
CEPAN 4	0.37	25	30	60	54	37
CEPAN 5[c]	0.31	25	30	60	53	39
CEPAN 6	0.36	43	30	60	154	127
CEPAN 7	0.36	25	30	40	28	15
CEPAN 8	0.31	43	30	40	49	35
CEPAN 9	0.38	43	30	50	71	52
CEPAN 10	0.37	43	30	70	188	156

[a] $GP_1\% = (W_{\text{CEPAN}} - W_{\text{CE}}) \times 100/W_{\text{CE}}$
[b] $GP_2\% = (W_{\text{CEPAN}} - W_{\text{CE-A}}) \times 100/W_{\text{CE-A}}$
[c] For the synthesis of this sample was used cellulose with DP = 490

For similar reasons, no tertiary amine has been added to the reaction medium in order to entrap HCl and further shift the reaction to the right.

Ten samples of CEPAN (see Table 2) have been prepared, as described in Section 2, following steps (a) and (b): the average value of DS found after step (a) has been 0.33 ± 0.06, which indicates a good reproducibility of the derivatization procedure. The cellulose degree of polymerization has been settled at ~250, except for a single experiment (see Table 2, CEPAN 5), where CE with DP~490 has been used.

Among the large choice of free-radical initiators, AIBN has been selected for its structural similarity to PAN repeat unit. The amounts of AN and AIBN added to the CE-A solutions have been taken in order to have an AN/AIBN molar ratio = 30, except for experiments leading to CEPAN 1 and 2 (Table 2) where the above ratio has been fixed at 50. Moreover, the AN/-A (acryloyl groups) ratio was varied between 10 and 43, and the reaction temperature between 40 and 70°C, respectively. The upper temperature limit of 70°C has not been passed to avoid thermal degradation of PAN. At this temperature the half-life of AIBN in DMF is 186 min (Kulkarni et al., 1979).

The last two columns on Table 2 give the w/w percent of grafted PAN (GP%) as referred to the weight of the starting CE (GP_1%) and to the weight of the CE-A (GP_2%).

From the full set of data the following observations can be drawn: grafted PAN increases with the increase of the ratio AN/-A in the whole temperature range. In fact, by comparing the samples CEPAN 4 and 6 ($T = 60$°C), and CEPAN 7 and 8 ($T = 40$°C), in both cases the increase of AN/-A ratio from 25 to 43 causes a rise of GP_1% and GP_2%. With regard to T effects, data for samples CEPAN 6, 8, 9 and 10 are reported in Fig. 2 as functions of $1/T$: curve *a* describes values of GP_1% vs. $1/T$; curve *b* describes values of GP_2% vs. $1/T$.

The ratio AN/AIBN has a rather poor influence on the grafting reaction, as shown by CEPAN 2 and 3, where the increase of the above ratio from 30 to 50 causes only a small decrease of both GP_1% and GP_2%.

Finally, variation of CE molecular weight does not affect the amount of grafted PAN as shown by comparing CEPAN 4 (DP = 250) to CEPAN 5 (DP = 490).

The above considerations are strictly valid only assuming that CEPAN is a neat product, i.e. if the extraction of PAN homopolymer is really effective. Thus, some SEC measurements have been specifically performed on a few samples, before and after DMF extraction, and on the fractions soluble in DMF.

The SEC solvent was DMAc/5% LiCl and the reference standard *o*-dichlorobenzene. As an example, Fig. 3a–c gives the results related to sample 5. The SEC chromatogram (Fig. 3a) refers to the whole product of the synthesis: two peaks at 18 and 23 min are evident. Fig. 3b refers to the extracted material and shows only one peak at 23 min, corresponding to neat PAN, as evidenced by the i.r. spectrum of the collected material. Finally, Fig. 3c, corresponding to the residue after DMF extraction (CEPAN), shows only the peak at 18 min. The comparison of the three chromatograms confirms the separation efficiency of PAN homopolymer from the copolymer CEPAN by using DMF under reflux conditions (see Section 2).

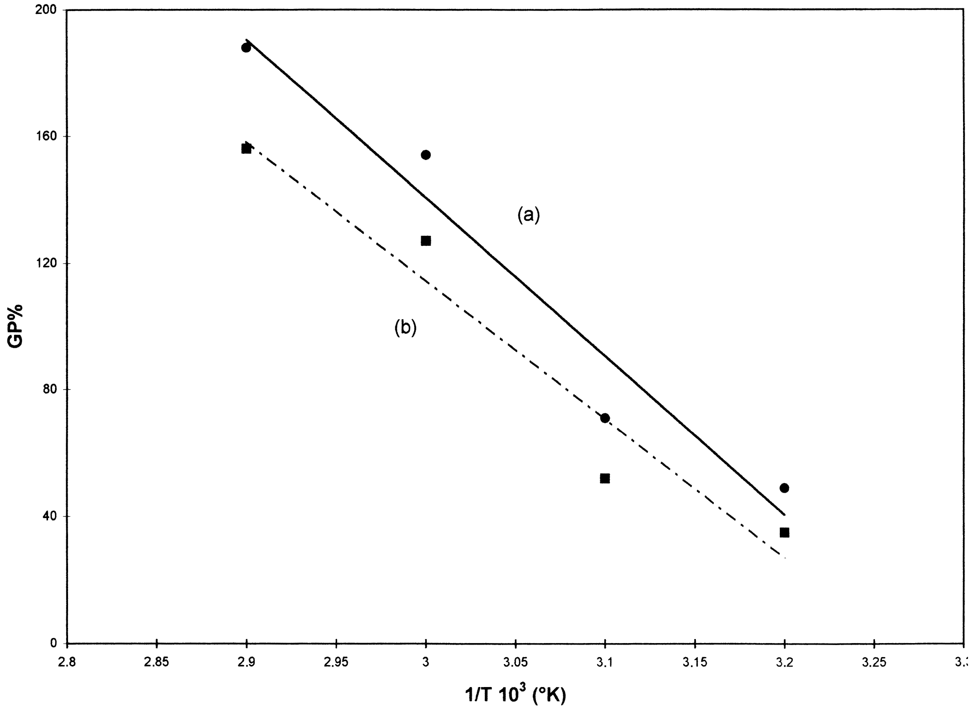


Fig. 2. Percent of grafted PAN versus temperature of reaction.

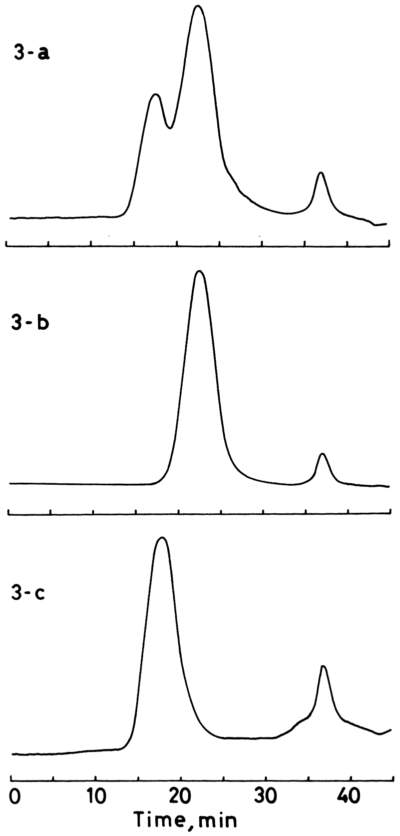


Fig. 3. SEC chromatograms of 2% solutions in DMAc/3% LiCl: (a) product of the synthesis (CEPAN + PAN); (b) material extracted by DMF (PAN); (c) residue after DMF extraction (CEPAN).

The i.r. spectrum of neat CEPAN evidenced a peak at 2243 cm^{-1}, characteristic of the –CN stretching band.

^{13}C n.m.r. spectra of CEPAN dissolved in DMAc/5% LiCl have been studied to clarify the reaction mechanism. Fig. 4 shows the spectrum of a solution containing ~10% of CEPAN 8, in the range of chemical shifts higher than 50 ppm. First of all, let us examine the range of 50–110 ppm, where the signals of the carbon atoms belonging to the glucosidic ring fall: the peaks of carbons C_1 and C_4 appear at 106 and 82 ppm, respectively, as for pure cellulose. The comparison of the peaks at 79 (C_3/C_4) and 77 (C_2) ppm with the corresponding ones observed for neat cellulose (Nehls et al., 1995) clearly indicate that esterification also does not involve the above carbon atoms. On the contrary, the original peak of C_6 at 63 ppm for neat CE is now split, appearing also at 76 ppm: the above splitting, already observed for other cellulosic esters (Nehls et al., 1995), provides clear evidence for the preferential esterification reaction on C_6.

Attribution of signals above 110 ppm has been performed by using the program SpecInfo 3.1.6: different hypotheses for the copolymer structure have been suggested and the computer program, on the base of its data bank, provided the corresponding spectra. By comparison with the experimental spectrum of CEPAN, the following conclusions can be drawn: (1) the peak at 123 ppm pertains to –CN groups, belonging both to the repeat units of PAN and to the initiator; (2) the signal at 166 ppm corresponds to the carbon atom of the ester function; (3) the peaks at 131 and

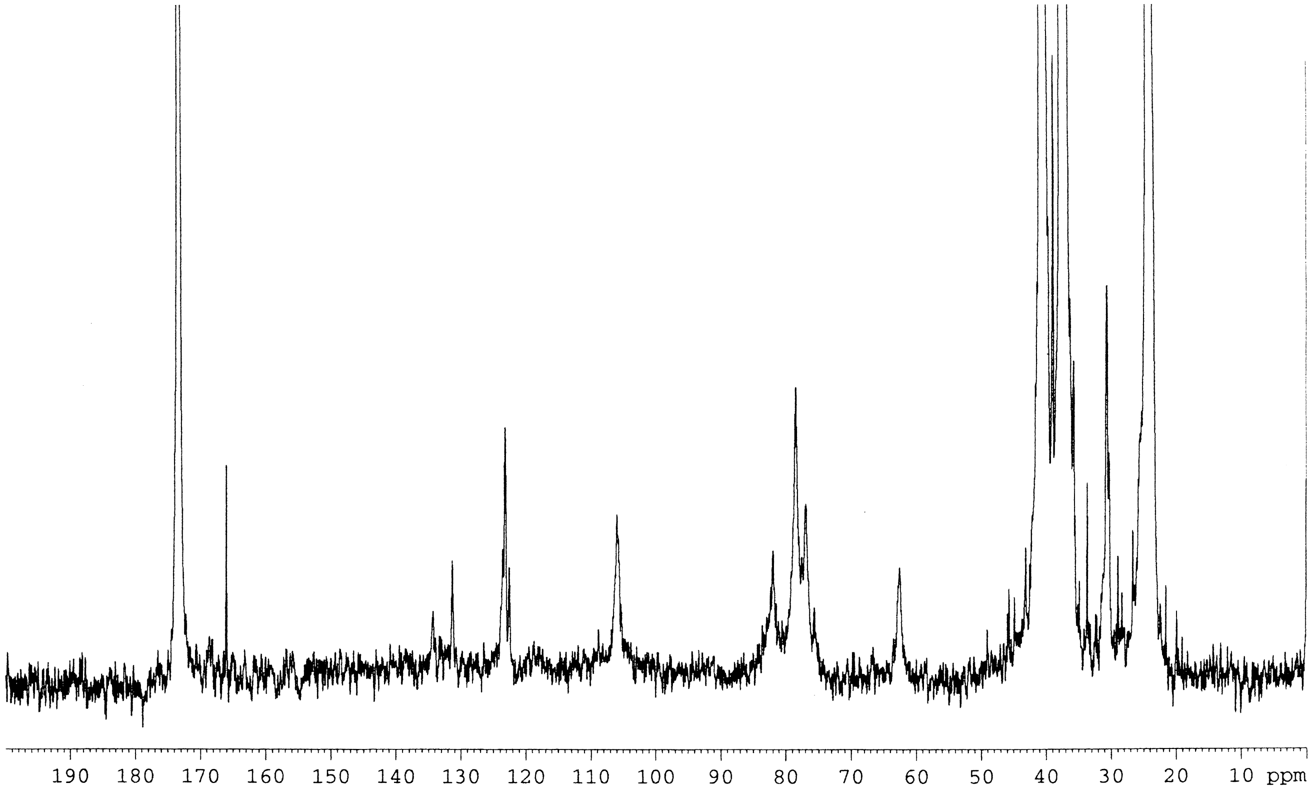


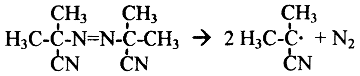
Fig. 4. ^{13}C n.m.r. of a 10% solution of pure CEPAN in DMAc/5% LiCl.

134 ppm correspond to residual unsaturated carbon atoms of the –A groups, thus demonstrating that not all double bonds reacted with AN.

On the basis of the above data, the following reaction mechanism seems the most probable:

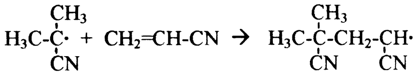
3.1. Initiation

Free radical initiator decomposition:



$$H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}N{=}N\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_3 \rightarrow 2\,H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\cdot + N_2$$

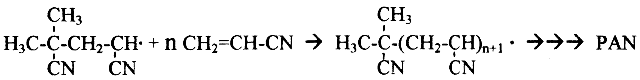
Addition of AN monomer to the primary radical:



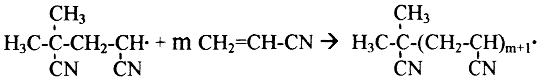
$$H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\cdot + CH_2{=}CH\text{-}CN \rightarrow H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\underset{CN}{CH}\cdot$$

3.2. Propagation

Formation of PAN homopolymer:

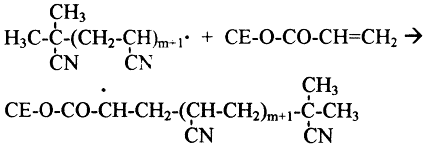


$$H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\underset{CN}{CH}\cdot + n\,CH_2{=}CH\text{-}CN \rightarrow H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2\text{-}\underset{CN}{CH})_{n+1}\cdot \rightarrow\rightarrow\rightarrow \text{PAN}$$

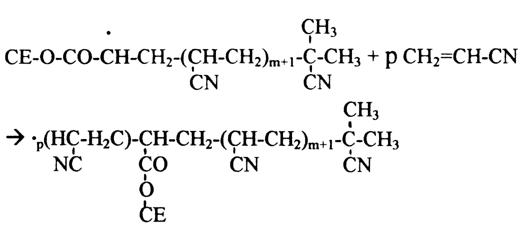


$$H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_2\text{-}\underset{CN}{CH}\cdot + m\,CH_2{=}CH\text{-}CN \rightarrow H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2\text{-}\underset{CN}{CH})_{m+1}\cdot$$

formation of CEPAN copolymer:

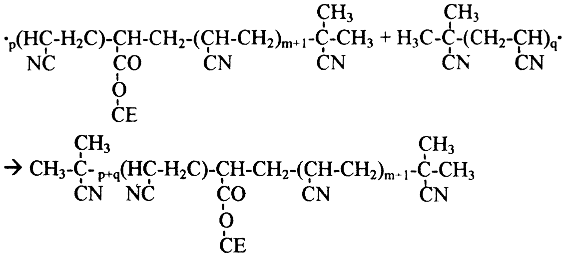


$$H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2\text{-}\underset{CN}{CH})_{m+1}\cdot + CE\text{-}O\text{-}CO\text{-}CH{=}CH_2 \rightarrow$$
$$CE\text{-}O\text{-}CO\text{-}\overset{\cdot}{CH}\text{-}CH_2\text{-}(\underset{CN}{CH}\text{-}CH_2)_{m+1}\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_3$$



$$CE\text{-}O\text{-}CO\text{-}\overset{\cdot}{CH}\text{-}CH_2\text{-}(\underset{CN}{CH}\text{-}CH_2)_{m+1}\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_3 + p\,CH_2{=}CH\text{-}CN$$
$$\rightarrow \cdot_p(\underset{NC}{HC}\text{-}H_2C)\text{-}\underset{\substack{CO\\O\\CE}}{CH}\text{-}CH_2\text{-}(\underset{CN}{CH}\text{-}CH_2)_{m+1}\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_3$$

3.3. Termination



$$\cdot_p(\underset{NC}{HC}\text{-}H_2C)\text{-}\underset{\substack{CO\\O\\CE}}{CH}\text{-}CH_2\text{-}(\underset{CN}{CH}\text{-}CH_2)_{m+1}\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_3 + H_3C\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}(CH_2\text{-}\underset{CN}{CH})_q\cdot$$
$$\rightarrow CH_3\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}_{p+q}(\underset{NC}{HC}\text{-}H_2C)\text{-}\underset{\substack{CO\\O\\CE}}{CH}\text{-}CH_2\text{-}(\underset{CN}{CH}\text{-}CH_2)_{m-1}\text{-}\underset{CN}{\overset{CH_3}{C}}\text{-}CH_3$$

A final observation concerns the transformation of the weight increase into the corresponding number of acrylonitrile units grafted per acryloyl substituent. The values calculated on the basis of our data (DS and grafted PAN) may be considered underestimated, as a certain fraction of double bonds does not participate to the grafting process (see the above n.m.r. data).

Therefore, by taking as an example CEPAN 10, the number of AN units linked to each double bond of the cellulosic chain is at least 7, but can be significantly higher than that.

4. Conclusions

It can be inferred that our method of homogeneous grafting onto modified cellulose has been proven to be rather satisfactory. A neat product with controlled and reproducible characteristics has been achieved. Reaction parameters controlling the grafting of PAN chains onto acryloyl-modified cellulose, namely reaction temperature and monomer to initiator molar ratio, have been fully evaluated. The grafted PAN yield resulted, as compared to homopolymer, favoured by an increase of temperature as well as of monomer concentration. The extension of the present method to other monomers is under way and will be reported elsewhere (Bianchi et al., manuscript in preparation).

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