

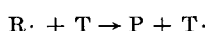
Graft Polymerization on Cellulose Derivatives by the Transfer Reaction

G. N. RICHARDS

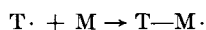
*British Rayon Research Association, Wythenshawe, Manchester, England**

INTRODUCTION

The transfer reaction in vinyl polymerization may be summarized as follows:



where $R\cdot$ is a growing polymer radical, P a "dead" polymer molecule, and T the transfer agent. The new radical $T\cdot$ is itself usually capable of initiating polymerization of monomer (M),



If T represents a pre-formed polymer, then the transfer reaction leads to production of a free radical site on the polymer molecule and hence to graft copolymerization. The transfer reaction can obviously occur to some extent with almost any substrate (T), but some attempts have been made to select polymers which have relatively high transfer constants and so favor graft polymerization by this mechanism. The method has been described for several synthetic polymers¹ and also for styrene and the 11-bromo-undecanoate of cellulose.² Furthermore, the transfer constants of both a brominated^{3a} and a thiol containing^{3b} polymer have been shown to be similar to the transfer constants of analogous model compounds and in each case have been used to prepare graft copolymers. It seemed probable therefore, that the relative reactivity of various cellulose derivatives in the transfer reaction could be derived from a study of model compounds containing the relevant groupings. We have recently determined the transfer constants of a series of methyl glucoside derivatives⁴ as model compounds for cellulose derivatives and the results suggested that a deoxy di-*n*-propylamino cellulose derivative with acrylonitrile and a deoxythio cellulose derivative with styrene should constitute very efficient systems for graft polymerization by the transfer reaction. This paper presents the results of a preliminary study of these two systems. An ethyl

cellulose has been used as base polymer in both cases in order to obtain organosoluble products.

EXPERIMENTAL RESULTS

Acrylonitrile, styrene, dimethylformamide, dioxan, and toluene were purified as described earlier.⁴ Unless otherwise stated, polymers were dried at 40° and 20 mm. over calcium chloride and then phosphoric oxide.

Preparation of Deoxydi-*n*-propylamino Ethyl Cellulose

Ethyl cellulose† was treated with toluene-*p*-sulfonyl chloride in pyridine to yield the partial toluene-*p*-sulfonate. Found: S, 1.99; OEt, 40.7%; corresponding to DS 0.16 and 2.26.‡

A 5.0-g. sample of this material was shaken with a mixture of 50 ml. of di-*n*-propylamine and 150 ml. of dimethylformamide to produce a clear, mobile gel which was heated in an autoclave at 150° for 20 hr. The resultant clear, amber-colored solution was added with stirring to 500 ml. of water to give a white precipitate which was reprecipitated from acetone solution with water, washed with water and dried. Yield: 4.8 g.; found: S, 0.02; N, 0.80; OEt, 42.9%; corresponding to DS 0.13 (amine) and 2.26 (ethyl).

Graft Polymerization of Acrylonitrile on Deoxydi-*n*-propylamino Ethyl Cellulose

The amino cellulose derivative (1.00 g.) was dissolved in 20 ml. of dimethylformamide in a Pyrex ampule, 0.01 g. of azobisisobutyronitrile and 5 ml. of acrylonitrile added and the solution frozen and degassed twice before sealing at 0.01 mm. After being heated in a bath at 60 ± 0.1° for 4 hr. the solution was cooled, diluted with 15 ml. of dimethylformamide, and then 60 ml. of ethanol were

† Type T.100, supplied by J. M. Steel and Co., London, England.

‡ The author is indebted to Dr. W. M. Corbett for this preparation.

* Present address: American Machine and Foundry Co., Blounts Court Research Laboratory, Sonning Common, Reading, England.

added slowly at room temperature (20°) with stirring. The resultant gelatinous precipitate (fraction A) was centrifuged and washed with 50 ml. of a 1:1 (v/v) mixture of ethanol and dimethylformamide, then with 20 ml. of ethanol, and dried (0.20 g.). The combined supernatant solution and washings from the first precipitation were further diluted with 200 ml. of water to produce a second precipitate (fraction B), which was filtered off, washed with water, and dried (1.30 g.).

Fraction B was next extracted by shaking for 1 hr. each at room temperature with two 50 ml. portions of acetone, leaving fraction (B₁) (0.90 g.) undissolved. The acetone extracts were diluted with 200 ml. of water to precipitate fraction B₂ as a white powder (0.38 g.). The analyses of fractions B₁ and B₂ are given in Table I.

TABLE I
Fractions from Graft Polymerization of Acrylonitrile on Deoxydi-*n*-propylamino Ethyl Cellulose

	B ₁	B ₂
Weight	0.90 g.	0.38 g.
Ethoxyl content	26.0%	37.7%
Nitrogen content	11.3%	2.3%
Polyacrylonitrile content	39% ^a 41% ^b	12% ^a 6% ^b

^a Calculated from ethoxyl content.

^b Calculated from nitrogen content (assuming amino content unchanged).

In a control experiment a sample of 0.1 g. of polyacrylonitrile (\bar{P}_w 400) dissolved in 5 ml. of dimethylformamide was completely precipitated by 7.5 ml. of ethanol.

Preparation of Deoxythio Ethyl Cellulose

The same toluene-*p*-sulfonated ethyl cellulose (5.00 g.) was swollen in 200 ml. of acetone, 2.0 g. of potassium thioacetate were added, and the mixture was heated at 120–130° in an autoclave for 24 hr. to yield a mixture of a brown solution and a gelatinous black solid. The solution was filtered and added to 500 ml. of water to produce a brown solid precipitate. This was washed with water and reprecipitated from acetone solution with water to give the acetyldeoxythio derivative (IV) as a straw-colored powder which was washed with water and dried. Yield: 3.02 g.; found: S, 2.5%; OEt, 41.5%.

A 1.00-g. sample of this material was dissolved in 50 ml. of dry methanol and the solution, together with 0.05 g. of sodium contained separately but in

the same vessel, was frozen and degassed twice before sealing at 0.01 mm. pressure. The solution and sodium were then mixed and kept at room temperature (ca. 20°) for 18 hr. with no obvious change in the viscosity of the solution. The resultant solution was added to 200 ml. of water to produce a pale yellow precipitate which was washed with water and dried at room temperature over phosphoric oxide. Yield: 0.69 g.; found: S, 2.4; OEt, 42.4%. A deoxythio ethyl cellulose of DS 0.16 (thiol), 2.26 (ethyl), requires S, 2.25; OEt, 44.6%.

The product was soluble in acetone immediately after preparation, but after keeping for 5 days at room temperature over phosphoric oxide at 20 mm. pressure, was only partly soluble in the same solvent, leaving an insoluble gel, which however, dissolved slowly (1 hr., 20°) on addition of an equal volume of a 5% solution of thioglycolic acid in 80% aqueous acetone.

In a separate deacetylation experiment, when no precautions were taken to exclude air, the solution had set to a rigid gel within 2 hr. after addition of sodium to the methanol solution of the acetyldeoxythio derivative (IV). The insolubilization in each case is attributed to oxidative crosslinking (see below).

Graft Polymerization of Styrene on Deoxythio Ethyl Cellulose

A 0.501-g. sample of deoxythio ethyl cellulose from the previous experiment (kept at room temperature for 5 days, see above) was shaken at room temperature (20°) for 2 hr. with 20 ml. of dioxan. The cellulose derivative was highly swollen and partly dissolved. After addition of 20 ml. of styrene the mixture was twice frozen and degassed before sealing at 0.01 mm. pressure, and then heated in a bath at 100 ± 0.5° for 7.5 hr. During heating, almost all of the gel dissolved. After cooling, the viscous solution was filtered from a trace of undissolved gel and added to 300 ml. of ethanol to produce a white precipitate which was washed with ethanol and dried (5.40 g.). The product was dissolved in 300 ml. of toluene and precipitated with *n*-hexane at room temperature (20°) in two fractions as follows:

- (A) 500–600 ml. of hexane; 4.46 g.; OEt, 2.20%
(B) 600–1000 ml. of hexane; 0.20 g.; OEt, 0.60%

A 3.806-g. sample of fraction A was next dissolved in 200 ml. of toluene and fractionally precipitated with ethanol at room temperature (20 ± 2°) as shown in Table II.

TABLE II
Fractions from Graft Polymerization of Styrene on Deoxythio Ethyl Cellulose

Fraction	Ethanol concn., %	Precipitate, g.	Ethoxyl content, %	Sulfur content, %	Insoluble in toluene, %	\bar{P}_w^a
0	26.0	0	—	—	—	—
1	28.6	0.09	11.8	—	—	—
2	31.0	0.06	6.0	<0.05	—	—
3	33.3	1.60	0.3	<0.05	0	1490
4	37.5	1.19	1.4	<0.05	4	2050
5	41.2	0.07	1.3	—	—	—
6 ^b	50.0	0.04	3.2	—	—	—
7	Evaporated to dryness	0.61	6.3	0.4	13	1710

^a Degree of polymerization determined from viscosity in toluene solution, calculated as polystyrene as described earlier.⁴

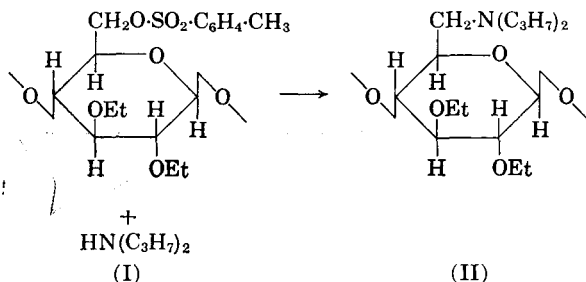
^b A sample of the supernatant solution was opaque but gave no further precipitate on addition of 1 volume of either ethanol, 1-butanol, or *n*-hexane.

Fractions 4–7 could not be completely redissolved in toluene—a small amount of colorless gel remaining in each case. The \bar{P}_w values are calculated on the soluble portion, after removal of the insoluble gel, the value for fraction 7 having qualitative significance only, since the viscosity constants for polystyrene were used in its calculation.

DISCUSSION

Graft Polymerization of Acrylonitrile on Deoxydi-*n*-propylamino Ethyl Cellulose

The preparation of the deoxydi-*n*-propylamino ethyl cellulose derivative (II) by treatment of an *o*-toluene-*p*-sulfonyl derivative (I) with di-*n*-propylamine is analogous to Haskins and Weinstein's preparation of a deoxybutylamino cellulose.⁵ Since the original ethyl cellulose was only partially esterified, the toluene-*p*-sulfonyl groups are probably predominantly situated at C₆ as shown.*

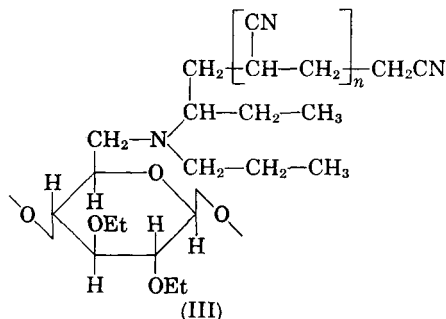


The transfer reaction consists of a catalyzed polymerization of acrylonitrile in a dimethylformamide solution containing the cellulose derivative (II). The isolation procedure described above is

* Dr. W. M. Corbett has verified this fact by sodium iodide exchange, which proceeds almost to completion with the toluene-*p*-sulfonyl groups in the ethyl cellulose derivative.

designed to precipitate polyacrylonitrile homopolymer (fraction A) and then to extract the unreacted cellulose derivative (fraction B₂) from the copolymer (fraction B₁). Such a separation is not necessarily complete, but there seems little doubt that fraction B₁ in Table I consists mainly of a graft copolymer of polyacrylonitrile on the cellulose derivative (II).

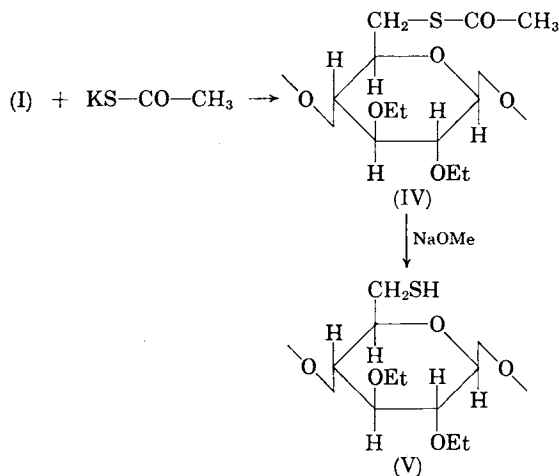
By analogy with the previous results on model compounds⁴ the transfer reaction with polyacrylonitrile radicals will occur predominantly at the tertiary amino group and the most probable mechanism of such a reaction is hydrogen abstraction from a methylene group in the α position to the amino nitrogen atom. Furthermore, since tri-*n*-propylamine has been shown⁶ to have a higher transfer constant than other tertiary amines, it seems probable that the propyl groups are involved in the reaction, rather than the C₆ methylene group. If this is the case then the graft copolymer would have the structure shown (III)



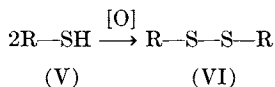
Deoxythio Ethyl Cellulose

The preparation of the deoxythio ethyl cellulose is based on that of methyl 6-deoxy-6-thio- α -D-glucopyranoside.⁴ Unlike the analogous reactions with model compounds, however, the exchange of

the toluene-*p*-sulfonyl group in the cellulose derivative (I) with potassium thioacetate requires rather drastic conditions and a low yield (65%) of the acetyldeoxythio derivative (IV) was obtained. Milder conditions than those described above, failed to induce any reaction, whereas more drastic conditions produced very extensive degradation.



The deacetylation of (IV) to the thiol derivative (V) was carried out in vacuum. If air were not excluded at this stage the product separated from solution as an insoluble gel. Similarly, the product prepared in absence of air also became insoluble on keeping. This behavior is attributed to the formation of disulfide crosslinks (VI) by autoxidation of the thiol groups as shown, and this is confirmed by the observation that the insoluble material could be solubilized by thioglycolic acid, which is known⁷ to reduce disulfides to thiols.



The ethoxyl content of the product was rather lower than would be expected for the deoxythio ethyl cellulose (V) of DS 2.26 (ethyl), 0.16 (thiol), which would result from complete replacement of toluene-*p*-sulfonyl groups with deoxythio groups. It is probable therefore, that the exchange reaction (I \rightarrow IV) was incomplete and that the product still contains some toluene-*p*-sulfonyl groups.

Thiol derivatives of cellulose have previously been prepared by Izard and Morgan⁸ and appear to undergo oxidative crosslinking readily.

Graft Polymerization of Styrene on Deoxythio Ethyl Cellulose

The graft polymerization was effected by uncatalyzed polymerization of styrene in dioxan solution in the presence of the cellulose derivative (V). The latter was present partly as an insoluble gel at the beginning of the reaction but eventually passed into solution. After a preliminary fractionation with *n*-hexane from toluene solution, the product was fractionally precipitated from toluene solution with ethanol (Table II). The early fractions (1,2) represent very small amounts of a material of high ethoxyl content and were not further examined. The next fractions to be precipitated (3,4) represent the bulk of the material and consist essentially of polystyrene. The fraction 7 remaining dispersed in 1:1 (v/v) ethanol-toluene however, probably represents graft copolymers of polystyrene on ethyl cellulose. The ethoxyl content corresponds to a copolymer of 14% ethyl cellulose (DS 2.26) and 86% polystyrene. No solvent mixture was found which would completely redissolve fractions 4 or 7. This insolubilization is presumably due to some unidentified form of crosslinking, either polar or covalent, subsequent to precipitation.

The transfer constant of the deoxythio cellulose derivative cannot be calculated from the available results for several reasons. The thiol content of the cellulose derivative (V) is not known because the replacement of toluene-*p*-sulfonyl groups in derivative (I) is probably incomplete (see above); also some thiol groups are involved in disulfide crosslinking and the transfer constant of a disulfide,⁹ like that of a toluene-*p*-sulfonate,⁴ is very small compared with that of the corresponding thiol. Furthermore, the cellulose derivative (V) was not in solution at the beginning of the styrene polymerization and therefore some polystyrene formed without access to the thiol groupings. The observed \bar{P}_w of the polystyrene however (fraction 3, $\bar{P}_w = 1490$), is considerably less than that of the corresponding polystyrene ($\bar{P}_w = 3420$) prepared⁴ under identical conditions in the absence of the cellulose derivative, and this fact provides qualitative evidence that the derivative (V) is functioning as a transfer agent.

Graft polymerization by transfer to thiol groups should be particularly effective in grafting on wool, where some thiol groups are already present and additional groups are readily liberated by reduction, e.g., with thioglycolates.⁷ The polymerization of vinyl monomers in wool fibers to give nonextractible

polymers,¹⁰ probably involves graft polymerization by this type of transfer mechanism.

All Micro-analyses were performed by Mr. T. Masters

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Synopsis

The deoxy-di-*n*-propylamino (II) and deoxy-thio (V) derivatives of ethyl cellulose have been prepared. Catalyzed polymerization of acrylonitrile in the presence of (II) results in chain transfer between the polyacrylonitrile radical and the tertiary amino group, with subsequent graft polymerization. A copolymer of ca. 40% polyacrylonitrile grafted on ethyl cellulose was isolated by a combination of fractional precipitation and selective extraction. Polymerization of styrene in presence of (V) results in chain

transfer between the polystyrene radical and the thiol groups, with subsequent graft polymerization. Fractional precipitation of the product yielded a fraction whose ethoxyl analysis corresponds to a copolymer of 86% polystyrene grafted on ethyl cellulose.

Résumé

Les dérivés désoxy-di-*n*-propylamino (II) et désoxy-thio (V) de l'éthylcellulose ont été préparés. La polymérisation catalysée de l'acrylonitrile en présence de (II) conduit à un transfert de chaîne entre le radical polyacrylonitrile et le groupe aminé tertiaire, avec comme conséquence une polymérisation greffée. Un copolymère d'environ 40% de polyacrylonitrile greffé sur l'éthylcellulose a été isolé par précipitation fractionnée combinée à une extraction sélective. La polymérisation du styrène en présence de (V) conduit à un transfert de chaîne entre le radical polystyrène et les groupes thiols avec greffage subséquent. Une précipitation fractionnée du produit donne une fraction dont l'analyse en groupe éthylique correspond à un copolymère contenant 86% de polystyrène greffé sur l'éthylcellulose.

Zusammenfassung

Es wurden die Desoxy-di-*n*-propylamin- (II) und Desoxy-thio-derivate (V) von Äthylcellulose dargestellt. Die katalysierte Polymerisation von Acrylnitril in Gegenwart von (II) ergab eine Kettenübertragung zwischen dem Polyacrylnitrilradikal und der tertiären Aminogruppe mit anschließender Pfropfpolymerisation. Durch Kombination von fraktionierter Fällung und selektiver Extraktion wurde ein Äthylcellulose-Copolymeres mit ca 40% aufgepfropftem Polyacrylnitril isoliert. Polymerisation von Styrol in Gegenwart von (V) ergab eine Kettenübertragung zwischen dem Polystyrolradikal und den Thiolgruppen mit anschließender Pfropfpolymerisation. Fraktionierte Fällung des Produkts ergab eine Fraktion, deren Äthoxylanalyse einem Copolymeren von Äthylcellulose mit 86% aufgepfropftem Polystyrol entsprach.

Received February 9, 1961