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(54) **Internally plasticised cellulose
polymers**

(57) **Plasticised cellulose polymers**
comprise base polymer having a chain
of β -anhydroglucose units joined by
ether linkages, with at least one of
said units carrying at least one
chemically unreactive side chain

derived from an allylic monomer or a
vinyl substituted derivative of
ferrocene. The side chains are
normally formed by radiation grafting.

These internally plasticised
celluloses are useful in particular as
inhibitor coatings for rocket motor
propellants and in general wherever
cellulose polymers are employed.

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SPECIFICATION

Plasticised cellulose polymers

The present invention relates to internally plasticised cellulose polymers.

5 Base resins for plastics materials are commonly mixed with a relatively small proportion of a comparatively low molecular weight compound in order to improve the workability of the resin and to improve its properties in the longer term, e.g. to prevent it from shrinking and cracking. Such "plasticisers" are normally merely physically mixed with the base resin and are susceptible to loss therefrom by evaporation, migration or extraction. By attaching side chains of about the same size as such plasticiser molecules to the resin, the resin can be "internally plasticised" and the effect in this case is permanent since the plasticising side chains will not become detached from the resin molecule and so no loss of "plasticiser" can occur. 10

It will be appreciated that in a sense any side chain attached to, for example, the cellulose molecule will be a plasticising side chain, so that for example even ethyl cellulose can be said to be internally plasticised to a degree. However we have now found that a satisfactory plasticising effect is surprisingly obtained when even a relatively small amount of an allylic monomer is incorporated as a side chain into cellulose or cellulose polymers in general. Accordingly, the present invention provides cellulose polymers comprising a base polymer having a chain of β -anhydroglucose units joined by ether linkages, wherein at least one of the β -anhydroglucose units in the chain of the base polymer is substituted by at least one chemically unreactive (as herein defined) side chain derived from an allylic monomer or from a vinyl substituted derivative of ferrocene. 15 20

The monomers which are used, according to this invention, to give plasticising side chains in cellulose polymers, are all capable of undergoing radical addition reactions in which they will exhibit substantially only mono-molecular termination of the addition reaction. As a result, there is no tendency with these monomers for the polymer chain to become cross-linked by radical addition during the grafting process. Cross-linking of the polymer chains should be avoided since it leads to the formation of an intractable mass of material. It is a further requirement therefore that the plasticising side chains be "chemically unreactive" by which is meant that, apart from being capable of undergoing radical polymerization and exhibiting substantially only monomolecular termination as described previously, the side chains should also either contain no functional groups at all or only such groups as will not interact with each other or with the polymer backbone under the conditions of the grafting reaction. By these means cross-linking of the polymer is avoided. 25 30

Apart from mono-allylic monomers, diallylic compounds, e.g. diallyl terephthalate, may also be used as the monomer since these do not in practice undergo cross-linking. Exemplary mono-allylic compounds which can be used include allyl acetate, allyl hexanoate, allyl alcohol, allyl glycidylether and allyl phenol. 35

The side chains introduced into cellulose or cellulose polymers according to this invention, may be straight or branched chains and there is no particular limit on their size or number.

However, as a general rule, the side chains most suitably comprise from 5 to 30% by weight of the total polymer product weight, though plasticising effects may in some cases be observed with a lower proportion of side chain material. The length of the side chain or chains introduced will depend on the degree of polymerisation of the monomer: in the case of allylic monomers proper this is usually about 10 so that the minimum chain length will be about 30 to 60 carbon atoms. Relatively short side chains (less than about 100 C atoms) are generally preferred, since whilst these effectively plasticise the polymer, they also result in products which are completely soluble in certain solvents and which are tractable and easily worked. The position of attachment of the side chains in the case of the polymers of this invention has not been fully examined. However it seems likely that chains may be linked onto existing side chains or attached at free hydroxyl groups on the cellulose polymer backbone or most probably attached to carbon atoms in the β -anhydroglucose rings after breakage of C—H bonds. However the plasticising effect on cellulose polymers which results from the attachment thereto of side chains of the type described according to this invention is in no way affected by the position of attachment of the chains and therefore it is not necessary that any specific mode of attachment need be achieved. 40 45 50

Attachment of the "plasticiser" side chains may be effected by employing any of the standard techniques of radiation grafting. Thus, for example, the base polymer may be dissolved in a suitable solvent, which can be the monomer compound itself. The reaction is initiated by radiation from, for example, a cobalt 60 source, and the extent of the reaction can be controlled by altering the dose rate or the total radiation dose. The reaction can be performed in air, under nitrogen or in vacuo. When the reaction has been taken to a sufficient extent, the irradiation source is removed and the treated polymer may then be purified by a double precipitation into hexane or water to remove any untreated monomer compound. 55 60

The conditions under which the radical addition reaction is carried out are rather critical since degradation by chain scission can readily occur if the conditions are unsuitable. Several interrelated factors have to be considered in choosing the optimum reaction conditions for any given polymer, including the nature of the chain-forming monomer and of the solvent, and the nature and intensity of

the radiation source. It will be apparent that the several variable factors have to be determined anew for each polymer in order to achieve an optimum result and that no particular rules can be laid down. In general, however, it may be said that the total radiation dose preferably should not exceed 20 MR, otherwise chain scission is likely to occur, and that optimum dose will generally be of the order of 5 MR.

5 An advantage of producing internally plasticised cellulose polymers via a radical addition reaction 5 is that it is possible thereby to prepare modified ethyl cellulose polymers containing chemical groups which have no affinity for nitroglycerine. Exemplary of such groups are epoxide linkages. Incorporation of these into the ethyl cellulose gives a plasticised product in which both plasticiser migration and uptake of nitroglycerine may be prevented. such modified celluloses could be particularly useful 10 therefore as inhibitor coatings for rocket motor propellants as well as being generally useful wherever cellulose polymers are employed. 10

The invention will now be further described, by way of example only, by reference to some specific, internally-plasticised cellulose polymers and methods for preparing them.

EXAMPLE 1

15 2 g of ethyl cellulose (Grade N200 from Hercules Inc.) was dissolved in 20 g of allyl acetate in a 15 tube and the solution degassed on a high vacuum line. The tube was then sealed and the tube and contents were irradiated at a dose rate of 3.2 MR hr⁻¹ for 1.8 hours. On isolation and after purification by a double precipitation into hexane a 73% yield of polymer was obtained (based on the original weight of ethyl cellulose taken). The polymer was completely soluble in xylene confirming that cross-linking 20 reactions had been prevented. The polymer was examined by IR and NMR spectroscopy and by GPC and 20 was shown to contain grafted side chains. The softening point of the polymer was determined and the result is shown in Table 1. This shows that the side chains lower the softening point of the ethyl cellulose and clearly therefore act as effective plasticisers. Heat ageing trials were also carried out and showed that no loss of plasticiser occurred confirming that the plasticisers are chemically linked to the 25 base polymer. 25

EXAMPLES 2 and 3

The procedure of Example 1 was repeated except that allyl glycidyl ether (2.0 g) or allyl hexanoate (2.0 g) were used as the 'plasticisers' respectively. In the latter case, the evacuated tube was backfilled with nitrogen. Results are given in Table I.

30 EXAMPLE 4 30

2.0 g of ethyl cellulose (Grade N200) was dissolved in dioxan (2.0 g) and 0.4 g of allyl acetate added. The reactants were sealed into an evacuated tube and irradiated at 3.2 MR hr⁻¹ for 0.3 hours. Softening point measurements gave a value of 95—100°C for the product.

EXAMPLE 5

35 Example 4 was repeated except that dimethylformamide (20g) was used as the solvent and the 35 plasticiser was allyl glycidylether (0.6g). The reactants were irradiated for 16 hours at 0.34 MR hr⁻¹ in a sealed nitrogen filled tube and gave a modified polymer product having a softening point of 115—120°C.

TABLE 1

Example No.	Internal Plasticiser	Base Polymer/Plasticiser Weight Ratio	Solvent	Atmosphere	Total Radiation Dose (MR)	Softening Point (°C)
—	Commercial Ethyl cellulose (N200)	—	—	—	—	165—170
—	„ „	—	—	air	11.1	145—150
1	Allyl acetate	1/10	—	vacuum	5.75	145—145
2	Allyl glycidylether	1/1	—	„	5.0	95—100
3	Allyl hexanoate	1/1	—	nitrogen	5.0	115—120
4	Allyl acetate	10/1	dioxan	vacuum	1.0	95—100
5	Allyl glycidylether	3/1	DMF	nitrogen	5.75	115—120

DMF = Dimethylformamide.

CLAIMS:

1. A cellulose polymer comprising a base polymer having a chain of β -anhydroglucose units joined by ether linkages, wherein at least one of the β -anhydroglucose units in the chain of the base polymer is substituted by at least one chemically unreactive (as herein defined) side chain derived from an allylic monomer or from a vinyl substituted derivative of ferrocene. 5
2. A cellulose polymer according to Claim 1 wherein the at least one side chain comprises from 5 to 30% by weight of the total polymer product weight.
3. A cellulose polymer according to Claim 1 or 2 wherein the at least one side chain contains less than 100 carbon atoms.
4. A cellulose polymer according to Claim 3 wherein the at least one side chain contains between about 30 and 60 carbon atoms. 10
5. A cellulose polymer according to any preceding Claim wherein the allylic monomer is a monoallylic monomer.
6. A cellulose polymer according to Claim 5 wherein the monoallylic monomer is allyl acetate.
7. A cellulose polymer according to Claim 5 wherein the monoallylic monomer is allyl hexanoate, allyl alcohol, allyl glycidyl ether or allyl phenol. 15
8. A cellulose polymer according to any of Claims 1 to 4 wherein the allylic monomer is a diallylic monomer.
9. A cellulose polymer according to Claim 8 wherein the diallylic monomer is diallylic terephthalate. 20
10. A cellulose polymer substantially as hereinbefore described with particular reference to the Examples.
11. A method for preparing a cellulose polymer according to Claim 1 comprising:
- a. dissolving the base cellulose polymer in a suitable solvent,
- b. adding the allylic monomer or the vinyl substituted derivative of ferrocene to the solution, and 25
- c. irradiating the solution with ionising radiation.
12. A method according to Claim 11 wherein the solution is irradiated with 20MR or less of ionising radiation.
13. A method according to Claim 12 wherein the solution is irradiated with between about 3 and 6 MR of ionising radiation. 30
14. A method according to any one of Claims 11 to 13 wherein the solvent is the allylic monomer.
15. A method according to Claim 11 to 14 wherein the solution is irradiated *in vacuo*.
16. A method according to any one of Claims 11 to 14 wherein the solution is irradiated under an air of nitrogen atmosphere.
17. A method according to any of Claims 11 to 16 wherein after irradiation, the polymer is purified by precipitation into a liquid aliphatic hydrocarbon or into water. 35
18. A method according to Claim 17 wherein the liquid aliphatic hydrocarbon is hexane.
19. A method for preparing a cellulose polymer substantially as hereinbefore described with particular reference to the Examples.
20. An inhibitor coating for rocket motor propellants containing a cellulose polymer according to Claim 1. 40