Studies of Degradation and Stabilisation Mechanism of Poly (vinyl chloride)

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Submitted
in fulfilment of the requirements
of the degree of
Doctor of Philosophy
to the
Indian Institute of Technology, Delhi
March, 1979

DEDICATED TO MY

WIFE URMIL AND CHILDREN

SWEETY, DIMPLE & SUNNY

AND

PARENTS

ACKNOWLEDGEMENTS

The author wishes to express on record his deep sense of gratitude to Professor Dr. (Mrs) I.K. Varma, Professor of Polymer Science and Coordinator, School of Materials Science & Technology, Department of Chemistry, Indian Institute of Technology, Delhi, for her keen interest, painstaking guidance, constant encouragement and constructive suggestions at various stages without which the present work would not have been possible.

I take this opportunity to thank Professor R.D. Dua, Senior Professor and Professor J.C. Ahluwalia, Head of Chemistry Department, not only for providing laboratory facilities but also for their all out help as and when required.

I am indebted to Professor D.S. Varma, Senior Professor of Textile Technology Department and Professor V.B. Gupta, Head of Textile Technology Department for providing me facilities to carry out studies on instruments like gel permeation chromatograph and thermogravimetric analyser during the course of this work.

Thanks are also due to Mr. J.M. Sood, Senior Technical Assistant of Shri Ram Institute for Industrial Research, Delhi for providing me help in analysing the samples in Differential Thermal Analyser, installed at their end.

I am also grateful to all faculty members of Chemistry and Textile Technology Department for their keen interest and participation in the discussions from time to time.

It is my privilege and pleasure to acknowledge the assistance and cooperation rendered to me at different stages of work by Drs.(Mrs.) C.K. Geetha, (Miss) Veena both Research Associates, S. Patnaik and Messrs Saudagar Mal, N.K. Sharma, M.S. Chaudhary, K.R. Murti& B.S. Rao.

It will be absolutely unforgettable the financial, moral and even otherwise, help rendered to me by all relatives and friends during this period.

I owe my sincere thanks to the management of Shri Ram Institute for Industrial Research, Delhi for granting me three years' leave for carrying out this programme in IIT Delhi.

I shall be failing in my duty if I don't acknowledge the help rendered to me by Dr. R.T. Thampy, Ex-Director of Shri Ram Institute for Industrial Research, Mr. M.C. Gupta, Administrative Officer and Mr. R.P. Wasan, Senior Librarian, both of Shri Ram Institute, in various shapes during the course of this work.

My thanks are also due to I.I.T. Delhi for the award of research fellowship for this period.

Finally, I wish to thank Mr. Rajesh Arora for neat and accurate typing of the manuscript and Mr. N.L. Arora for tracing the figures.

K.K. SHARMA

ABSTRACT

Degradation of PVC is initiated from weak sites in the polymer backbone, and stabilisation can be affected by removal of such labile sites. Attempts have been made in the present work to stabilise PVC by Diels-Alder reaction and cationic graft copolymerisation. The possibility of Diels-Alder reaction between partially degraded PVC with alkyl maleates (diethyl, dibutyl and dioctyl maleates) and other suitable dienophiles was investigated. Such an adduct formation might de-activate the labile chlorine in polymer backbone, thus reducing the evolution of HCl. Discolouration of PVC will also be reduced, due to removal of conjugated double bonds. Based on rate of dehydrochlorination data, the order of stability of PVC was found as

Dioctyl maleate > diethyl maleate > dibutyl maleate

IR spectrum of PVC degraded in these solvents revealed the presence of additional band at 1744cm^{-1}, which has been explained on the basis of adduct formation. λ_{max} was observed at 325±2 nm which corresponded to ≃ 5 double bonds. Since the rate is not reduced in comparison to that in ethyl benzoate, it is quite possible that the adduct formation may be taking place at the conjugated double bonds away from allylic chlorine.

Degradation of PVC in ethyl benzoate in presence of maleic anhydride (MA), p-benzoquinone (BQ) and 9:10 anthraquinone at different temperatures was also studied. Rate and

electronic absorption spectra of samples degraded in presence of these additives revealed that all these additives are effective stabilisers at higher temperatures ($>200^{o}C$). IR spectrum of PVC degraded in presence of MA indicated two bands at 1787 cm^{-1} and 1744 cm^{-1} corresponding to carbonyl stretching of anhydride group. However, samples degraded in presence of quinones did not reveal any peak corresponding to carbonyl group. The reduction in rate as well as in absorption of the samples when degraded in MA is attributed to formation of Diels-Alder adduct between MA and degrading PVC. The reduction in rate in case of BQ and AQ was explained on the basis of radical addition reaction. Molecular weight distribution studies by gel permeation chromatography revealed both cross-linking and chain scission reactions. Therefore, molecular weight distribution of degraded PVC samples did not alter significantly.

PVC-g-polystyrene of various compositions were synthesised in nitrobenzene using $AlCl_3$ as cationic initiator. No degradation of PVC was observed under the conditions employed in cationic graft copolymerisation.

Initial dehydrochlorination of PVC, monomer, catalyst, and polymer concentration and reaction temperatures, had significant effect on % graft-on. The presence of grafts was confirmed by ir and DTA studies. Grafted samples were found to

be thermally more stable than PVC by rate of dehydrochlorination measurements, absorption studies, thermogravimetric analysis (TGA) and differential thermal analysis (DTA).

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