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Modification of Poly(vinyl Alcohol) through Reaction with Cp_2HfCl_2, Cp_2ZrCl_2, and Cp_2TiCl_2*

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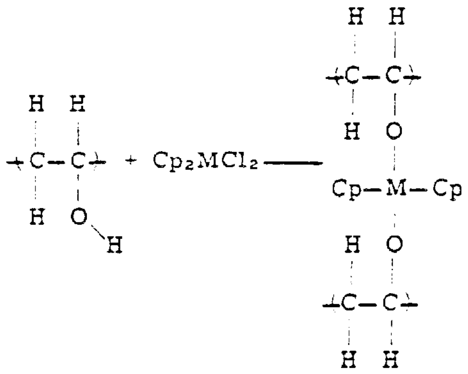
ABSTRACT

The modification of poly(vinyl alcohol) was effected through reaction with Cp_2HfCl_2, Cp_2ZrCl_2, and Cp_2TiCl_2 to give cross-linked products containing the following unit:



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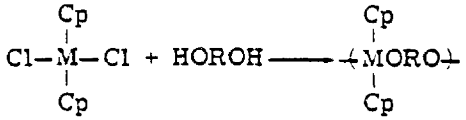
*Portions taken from the thesis of J.P. (1971).

Modification was effected by both the interfacial and solution routes. The thermal stability of the products is presented and discussed.

INTRODUCTION

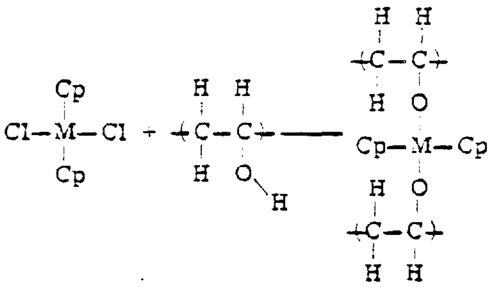
We have been investigating the synthesis of polymers containing metals in knowable positions in their backbone. Recently our work concerned the synthesis of Group IVB-containing products such as are illustrated by Structure I where M = Hf, Zr, and Ti [1, 2]:



$$\mathrm{Cl}-\overset{\mathrm{Cp}}{\underset{\mathrm{Cp}}{\mathrm{M}}}-\mathrm{Cl} + \mathrm{HOROH} \longrightarrow \left(\overset{\mathrm{Cp}}{\underset{\mathrm{Cp}}{\mathrm{M}}}\mathrm{ORO} \right) \qquad (1)$$

I

Other work of ours concerned the modification of commercially available polymers containing functional groups analogous to those utilized by us in the synthesis of products such as illustrated in Eq. (1) [3-6], believing that such modifications are simple extensions of our other work. Poly(vinyl alcohol), PVA, is such a polymer containing hydroxyl groups. Most work concerning the modification of PVA involves the esterification [7-10], sulfonation [11-14], and phosphorylation [15-19] of the hydroxyl group. These modifications utilized the melt and/or solution techniques. More recently analogous modifications were effected utilizing the interfacial technique [4, 6, 20-25]. We now report the initial modification of PVA utilizing Group IVB reactants as illustrated by



(2)

II

EXPERIMENTAL

Commercial PVA (99% hydrolyzed; Matheson, Coleman & Bell, Norwood, Ohio) with a weight-average molecular weight of about 63,000 by light-scattering photometory was used. The dicyclopentadienyl Group IVB dichlorides were used as received. Cp_2ZrCl_2 and Cp_2TiCl_2 were purchased from Alfa Inorganics, Beverly, Massachusetts, and Cp_2HfCl_2 from Strem Chemicals, Inc., Danvers, Massachusetts.

Polymerization procedures and equipment are similar to those described elsewhere [4, 26]. Briefly, aqueous solutions of PVA containing NaOH (equal to the theoretical maximum mole amount of chloride available from the Cp_2MCl_2) were added to rapidly stirred solutions containing $CHCl_3$ with added Cp_2MCl_2. The product rapidly precipitates from the reaction mixture and is separated by suction filtration. Since some unreacted PVA may also precipitate, the recovered solid is further washed by adding it to a beaker containing about 250 Ml water. This is set aside for 2 days, with continual mechanical stirring, whereupon it is again filtered. The filtrate contains only unreacted PVA as determined by IR spectroscopy.

The amount of unreacted PVA was determined by evaporating the aqueous phase (combined with the washings) using vacuum. Water was added to the solid, dissolving all but the PVA, which takes about 6 hr to go into solution. The mixture was filtered and solid PVA dried and weighed. From knowledge of the amount of unreacted PVA, the amount of Cp_2M moiety incorporated in the product was calculated based on a repeating unit of Structure II. A 50 mole % Cp_2M inclusion would result if each PVA-hydroxyl group were reacted.

IR spectra were obtained utilizing KBr pellets and a Beckman IR-10 or Perkin Elmer 237 B spectrophotometers. Spectra were consistent with inclusion of the Cp_2M moiety.

Thermal gravimetric analysis was conducted employing a 950 duPont TGA. Differential scanning calorimetry was carried out employing a DuPont 900 DSC cell fitted on a duPont 900 Thermal Analyzer Console. A linear baseline compensator was used with the DSC cell to insure a constant energy baseline. A Mettler H20T semimicro balance was employed for the DSC sample weighings. Measurements were obtained on samples contained in open aluminum cups to allow the free flow of volatilized gases away from the solid, thus more closely simulating the conditions under which

TGA studies were conducted. A flow rate (of both air and nitrogen) of about 0.3 liter/min gas was employed for both DSC and TGA studies. The samples were ground to powders to aid in obtaining reproducible results.

DISCUSSION AND RESULTS

There are several reasons for utilizing the Group IVB reactants employed. First, all are commercially available and compose a series in which only the metal is varied. Second, they are stable in air and relatively stable to hydrolysis. Third, all three are well-known commercial catalysts or cocatalysts and might impart such qualities to products derived from them. Fourth, some polymers from these reactants have shown good thermal stability [1, 2, 27-29]. Fifth, we have found these reactants to be quite reactive to attack by diols, diamines, dithiols, and dicarboxylates in previous studies employing the interfacial technique [1, 2, 27-29].

Reaction is rapid, being essentially complete within 30 sec. Yield is high and inclusion is in the medium to good range. Sample results appear in Table 1. Yields varied no more than ±2% for stirring times of 30, 60, and 180 sec.

The products are presumably cross-linked. This is in agreement with the insolubility of the products in all the solvents tried.

Thermograms of the products are reproduced in Figs. 1 to 3. Several general results are apparent. First, as desired, the thermostability of the products, measured by weight retention, is enhanced in comparison to that of the unmodified product. Several of the products show greater than 70% weight retention to 900°C in both air and N_2. For many industrial polymer applications the amount of nonmetal remaining after heating in air is important. The end product from the decomposition of the Group IVB polymers in air after prolonged heating at high temperatures (1000°C) is MO_2. To calculate the minimum remaining nonmetal, one may simply calculate the percentage MO_2 compared to the overall weight of a unit. Based on a product of Structure II, the following percentages were calculated: TiO_2 = 31%, ZrO_2 = 40%, and HfO_2 = 54%. Thus at 900°C the following minumum percentages of nonmetal are found in air for the modified PVA: Cp_2TiCl_2 = 10%, Cp_2ZrCl_2 = 18%, and Cp_2HfCl_2 = 10%. Thus, while the weight retention is good in air, it may not be good with respect to nonmetal weight retention. IR spectra of analogous products after

TABLE 1. Products from PVA[a]

Organometallic reactant	Yield[b] (%)	Mole % organometallic reactant included in product	Physical appearance and texture
Cp_2TiCl_2	96	41	Light brownish yellow, flexible, fiberlike
Cp_2ZrCl_2	80	37	White, tough, brittle
Cp_2HfCl_2	81	37	Light gray, powdery

[a] Reaction conditions: PVA (0.003 mole) with NaOH (0.006 mole) in 50 ml water condensed with 0.003 mole of the organometallic reactant in 50 ml $CHCl_3$ with stirring at 17,500 rpm (no load) for 30 sec stirring time at 25°C.

[b] Yields varied no more than ±2% for stirring times of 30, 60, and 180 sec.

heating show the presence of detectable amounts of the organic moieties but the bands are broadened and less intense.

Second, above about 300°C the DSC thermograms become dissimilar. Degradation in N_2 is occurring via an endothermic route whereas degradation in air is occurring via an exothermic route. Such situations have been explained as being characteristic of degradation in air occurring by an oxidative pathway [30].

Third, weight retention is greater in N_2 than in air. This appears to be normal for Group IVB products [31, 32].

Fourth, DSC thermograms are the same in air and in N_2 to about 300°C, indicating similar, nonoxygen associated transitions. The endothermic portions are not accompanied by weight loss to about 150°C whereas the exothermic portions are accompanied by weight loss in the 150 to 300°C region.

Fifth, modification of PVA with Group IVB reactants results in a complete change in the thermal transitions of the PVA. Nowhere in the thermograms of the products are there endo- or exothermic portions corresponding to that of PVA itself. This is consistent with a high degree of inclusion of the Cp_2M moiety.

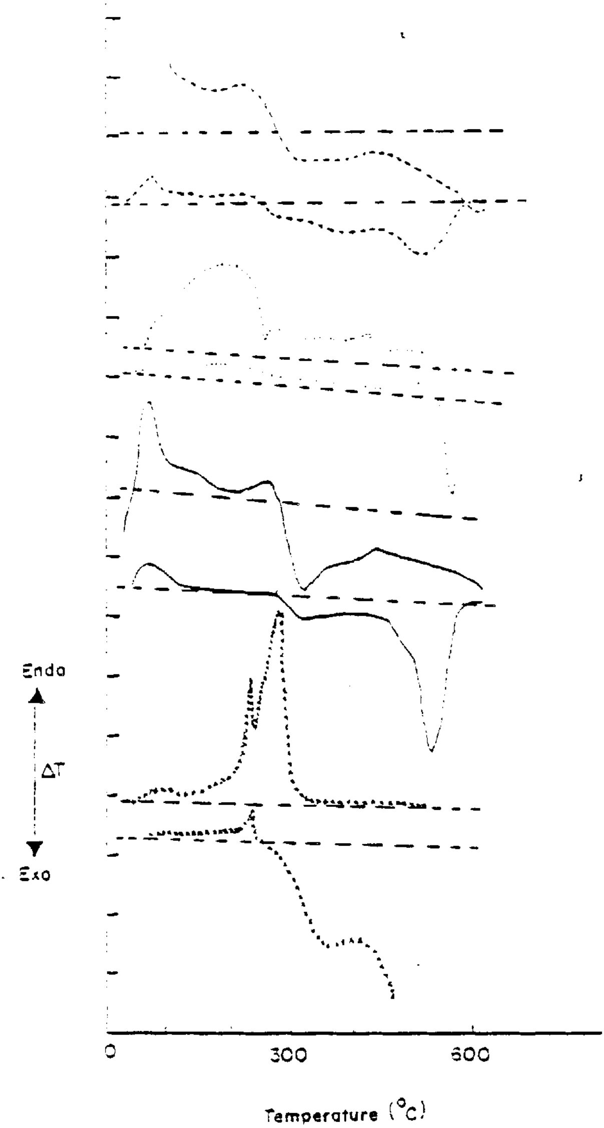


FIG. 1. DSC thermograms for the products from the condensation of PVA with Cp_2HfCl_2 (- -), Cp_2ZrCl_2 (· ·), Cp_2TiCl_2 (——), and PVA (××) itself at a heating rate of 30 C°/min with a N_2 and air purge of 0.3 lpm with a ΔT reading of 0.1°C/in. (0.004 mV/in.) in N_2 and 1.0°C/in. (0.04 mV/in.) in air except for PVA itself where the ΔT readings are 0.2°C/in. in N_2 and 0.5°C/in. in air. Each marked unit represents 1 in. (on the ΔT scale). The — — line represents ΔT = 0, i.e., no heat gained or lost. Sample weight was 0.00100 g.

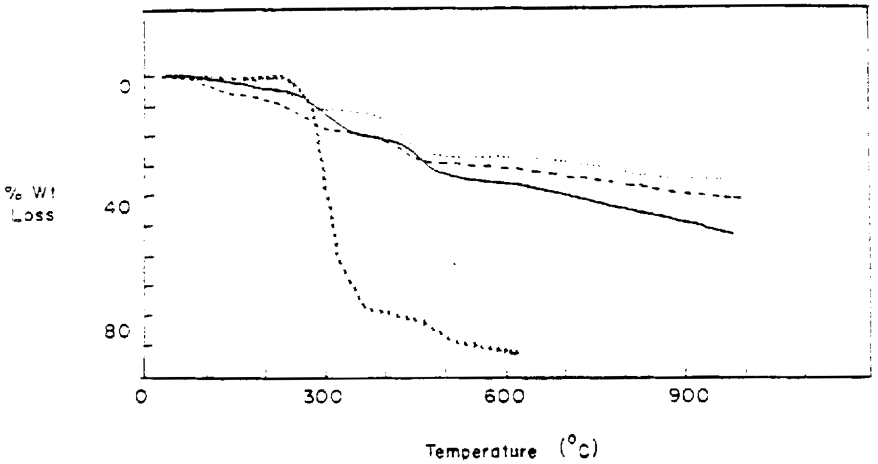


FIG. 2. TGA thermograms for the products listed in Fig. 1 in N_2.

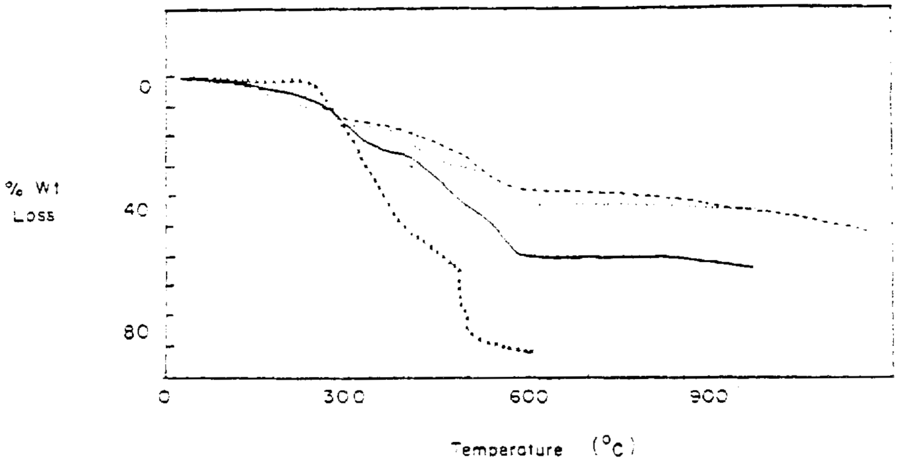


FIG. 3. TGA thermograms for the products listed in Fig. 1 in air.

REFERENCES

[1] C. Carraher and S. Bajah, Polymer, 14, 43 (1973).
[2] C. Carraher and S. Bajah, J. Polym. Science, Part A-1, In Press.
[3] C. Carraher and J. Piersma, Makromol. Chem., 152, 49 (1972).

[4] C. Carraher and L. Torre, J. Polym. Sci., Part A-1, 9, 9751 (1971).

[5] C. Carraher and L. Wang, Makromol. Chem., 152, 43 (1972).

[6] C. Carraher and L. Torre, Angew. Makromol. Chem., 21, 207 (1972).

[7] O. Wichterle, German Patent 1,065,621 (1959).

[8] M. Dime, A. Carpox, and S. Maxim, Rev. Roum. Chim., 13, 485 (1968).

[9] M. Shiraishi, Japanese Patent 17,582 (1968).

[10] G. Smirnov, I. Okhrimenko and L. Mashlyakorski, Zh. Prikl. Khim., 41, 2304 (1968); Chem. Abstr., 70, 30,115.

[11] A. deCat, J. Lemmerling, and A. Van Paesschen, British Patent 976,392 (1964).

[12] E. Korneva, O. Smirnov, and V. Urarova, Zh. Prikl. Khim., 39, 1876 (1966).

[13] D. Reynolds and W. Kenyon, J. Amer. Chem. Soc., 72, 1584 (1950).

[14] O. Klimova and V. Datsenko, Zh. Prikl. Khim., 33, 2582 (1960).

[15] N. Kulikova, M. Androsova, and N. Orlov, Zh. Prikl. Khim., 40, 2318 (1967).

[16] N. Volgina, I. Seregina, L. Vol'f, Y. Kirilenko, S. Borisor, E. Nifant'er, Zh. Prikl. Khim., 41, 2563 (1968); Chem. Abstr., 70, 48,534.

[17] N. Sviridovaard and K. Tammik, Zh. Prikl. Khim., 41, 2563 (1968); Chem. Abstr., 70, 48,534.

[18] N. Brace, U.S. Patent 2,733,229 (1956).

[19] Y. Motozato, H. Egawa, H. Maegaki, and K. Kunitate, Kogyo Kagaku Zasshi, 59, 479 (1966).

[20] Y. Motozato, R. Tamura, and H. Egawa, Japanese Patent 6,970 (1957).

[21] V. Laurishehev, Y. Bokov, and N. Vikulina, Russian Patent 194,310 (1967).

[22] Y. Tsuda, Japanese Patent 20,138 (1965).

[23] T. Shermergon and Y. Kamardin, Vysokomol. Soedin., 7, 2156 (1965).

[24] Y. Kamardin, I. Shermergorn, and I. Magdeer, Vysokomol. Soedin., Ser. B, 9, 419 (1967).

[25] M. Tsuda, U.S. Patent 3,329,564 (1967).

[26] C. Carraher, J. Chem. Educ., 45, 462 (1968).

[27] C. Carraher, Eur. Polym. J., 8, 215 (1972).

[28] C. Carraher and R. Nordin, J. Polym. Sci., Part A-1, 10, 521 (1972).

[29] C. Carraher and J. Reimer, Polymer, 13, 153 (1972).
[30] E. Ehlers and K. Fisch, "International Symposium on Polymer Characterization." Appl. Polym. Symp., 8, 171 (1969).
[31] C. Carraher, Unpublished Results.
[32] C. Carraher, Amer. Chem. Soc., Org. Coatings Plastics Chem., 31, 338 (1971).

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