

Organometallic Polymers. V. Synthesis and Properties of Metallocene-Modified Polymers

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Synopsis

The reaction of metallocenes with solutions of polydienes and halogenated polymers, under Friedel-Crafts conditions, has now been applied to the surface modification of solid polymer films. The reaction of ferrocene with chlorinated polyethylene films appears to proceed by a fast substitution step followed by a slower diffusion-controlled step. The stress-strain curves of surface-modified films, as well as of solution-cast polymetallocene films, have been examined by means of a bursting-strength apparatus. The weathering behavior of metallocene-modified polymers has been studied in both natural and accelerated conditions. Studies on the effect of ageing on composition and properties by spectrophotometric and mechanical measurements indicate that the photooxidative resistance of polymers is improved significantly by metallocene modification. Additionally, modified films have been found to be effective as clear shields for the protection of vulnerable substrates against photodegradation. The observed darkening of the irradiated films could be due to a thermal reaction between metallocene and photolytically generated macroperoxides.

INTRODUCTION

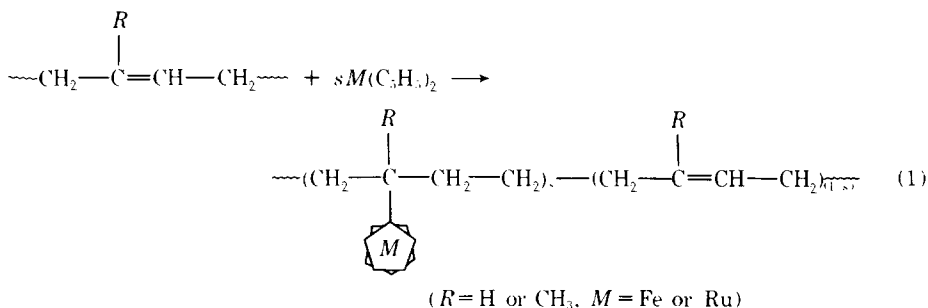
Ultraviolet light represents only a small fraction of the solar radiation reaching Earth's surface, yet it is considered the main single factor in the degradation of plastics in outdoor conditions.¹ Since the iron group metallocenes are known to absorb in the ultraviolet region of the spectrum as well as to display a remarkable photostability,² one may expect polymetallocene films to be potentially useful as photoresistant ultraviolet barriers. The advantages of built-in ultraviolet absorbers over the conventional additives have already been discussed in the literature.^{3,4}

In two recent reviews of the polymetallocene literature^{5,6} there is no mention of rubbery (low-glass transition temperature T_g), high molecular weight materials. This is not very surprising, considering that metallocene monomers impart rather high T_g to polymers and that they do not readily copolymerize with common plasticizing monomers, such as olefins or dienes. The brittleness of the available polymetallocenes—produced either by polycondensation or by polyaddition—would prevent their use in the form of thin films. To obtain materials suitable for such use, we tried a different synthetic approach, namely the chemical modification by metallocene compounds of low- T_g polymeric substrates.

Ferrocene and some of its derivatives have been shown to undergo electrophilic alkylation, similar to benzenoid aromatic compounds.⁷ In the previous two papers of this series^{8,9} we described modification processes involving polymeric substrates capable of alkylating the metallocene nucleus, usually in the presence of a Friedel-Crafts catalyst. Diene polymers are believed to react with metal-

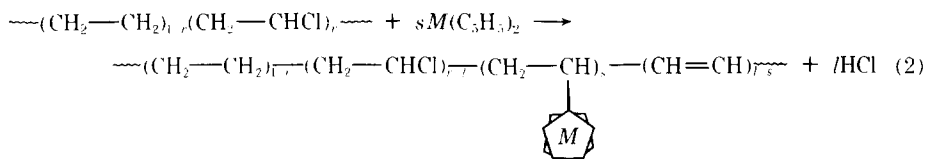
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locene according to the following scheme:



Various butadiene polymers ($R = \text{H}$) and natural rubber ($R = \text{CH}_3$) were employed as substrates, the modifiers being ferrocene, *n*-butylferrocene, *t*-amylferrocene, and ruthenocene. In the case of a high molecular weight *cis*-polybutadiene, the soluble reaction products contained up to 43% ferrocene.

Metallocenes were also reacted with a number of halogen-containing polymers,⁹ such as chlorinated polyolefins and poly(vinyl chloride). Soluble polymers of up to 62% ferrocene could be obtained in this way, but substitution was, as a rule, accompanied by dehydrohalogenation. The process can be depicted schematically as follows:



The ratio between dehydrohalogenation and substitution $(l-s)/s$ was found to be higher with poly(vinyl chloride) than with chlorinated polyethylenes. When the polymer was dissolved in molten ferrocene it underwent substitution even without addition of a Friedel-Crafts catalyst.

Whereas in our previous work we have investigated reactions of metallocenes with polymers in solution, we wish to describe here a modification process by which preformed polymer films were surface reacted with metallocenes. In addition we shall report on the mechanical properties and weathering behavior of polymetalocene films, both surface-substituted and solution cast.

EXPERIMENTAL

Materials

The polyethylene films employed were made of Ipethene 112 from Petrochemical Industries Ltd., Haifa. The other starting materials had been described previously.^{8,9}

Syntheses

The chlorination of polyethylene films was carried out in glacial acetic acid¹⁰; the reaction conditions and characteristics of the products are tabulated in Table I.

The surface substitution of halogen-containing films was carried out in a thermostatic bath filled with solution of the metallocene and catalyst, under nitrogen atmosphere. The films, sandwiched between polypropylene screens, were immersed into the bath for a predetermined reaction time and subsequently washed with a solution of ascorbic acid (1%) in methanol, soaked for 24 hr in dichloromethane and for another 6 hr in methanol. Finally the films were vacuum-dried overnight, at 40°.

The preparation of solution-substituted polyethylenes and polybutadienes has already been reported.^{8,9} Films of the metallocene-containing polymers were cast from toluene-mesitylene (9:1) solution on cellophane and dried at 28° in a slow stream of nitrogen. The dry films could be peeled off after wetting the cellophane with water. To remove traces of solvent the films were soaked overnight in methanol and then dried under vacuum.

Weathering

The accelerated weathering tests were performed by means of a 300 W Sunlamp (Osram Ultra-Vitalux Radiator Gur-53), preaged for 50 hr. The test specimens were placed radially on a turntable centered 20 cm below the sunlamp, in a circle of the same size as the lamp's diameter. Ventilation of the device was adjusted to maintain a turntable temperature of 60° ± 1°. The lamps were changed after 450 hr.

The outdoor weathering tests were conducted on the roof of the Chemistry building on the Technion Campus in Haifa, between April and September 1973. The films were mounted on a rack facing south at an angle of 45°. ¹¹ Radiometric data were received from Beit Dagan Meteorological Station.

Data were collected from measurements performed at intervals of about 1, 2, 4, 10, 20, and 29 days in the accelerated tests and fortnightly in the outdoor weathering tests.

TABLE I
Surface-Chlorination of Polyethylene Films (Ipethene 112)

Film gauge (mm)	Chlorination ^a time (min)	Final chlorine content (%)	Mechanical properties	
			Bursting strength (atm)	Distention (%)
0.040	0	0	2.4	38
0.040	60	7.3	2.05	75
0.040	70	21.0	2.65	125
0.040	100	27.8	3.1	105
0.100	0	0	5.3	38
0.100	60	5.5	4.3	55
0.100	70	16.7	4.3	75
0.100	100	22.6	5.0	88
0.100	100 ^b	8.25	4.0	63

^a Chlorination in acetic acid, at 70°; flow of chlorine 4.6 dl/min.

^b Chlorinated in gaseous chlorine atmosphere at 67°, 1.2 dl/min Cl₂.

Characterization

The spectral measurements of films were carried out with Perkin-Elmer Spectrophotometers, Model 137 (UV) and Model 257 (IR), using air as reference. The analytical methods have already been described.⁸

For the mechanical testing of polymers a bursting strength apparatus was built, similar to those used in paper¹²—and textile¹³—industries. This apparatus permitted the testing of circular film specimens as small as 11 mm in diameter. The pressure applied on the film was increased at a constant rate of 0.085 atm/sec and the height of the bulge formed was measured by means of a micrometer. The distention of the film under pressure, defined as the percent ratio between the area of the bulge and the initial exposed area of the specimen was calculated as a function of the bulge height.

RESULTS AND DISCUSSION

Surface-chlorinated polyethylene films treated with ferrocene solution, in the presence of Friedel-Crafts catalyst, became yellowish as a result of substitution. When plotting the metallocene content of films treated in this way against the square root of the reaction time, the process appears to consist of two distinct steps. In both cases illustrated in Figure 1, the ferrocene content increased in the first step rapidly up to about 6%. This step probably involved chloro functions located on or near the film's surface, which were readily available for substitution. The much slower increase of ferrocene content in the following step, proportional to the square root of time, suggested a diffusion-controlled process¹⁴—possibly taking place in the solvent-swollen amorphous region of the polymer.

Table II shows the effect of degree of chlorination of the substrate on the extent of ferrocenylation. The residual bursting strength and residual distention included in this table were calculated as the percent ratios between the respective properties of the film after and before ferrocenylation. Whereas the strength and elongation of these surface-treated films were only marginally affected, more extensive homogeneous substitution resulted in greatly changed mechanical properties. In Figure 2, curves g and f are the stress-strain curves of two solution-substituted polyethylene films. The much larger elongation of these polymers in comparison with polyethylene (curve e) was probably brought about

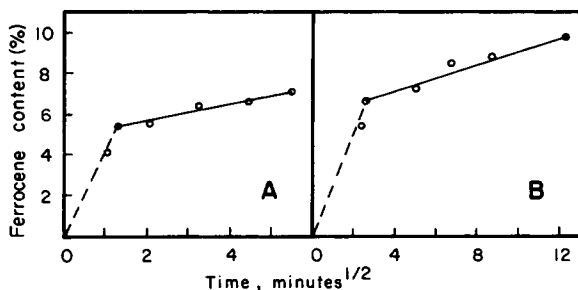


Fig. 1. Course of reaction between chlorinated polyethylene films and ferrocene, in presence of 0.36M AlCl_3 (Solvent: 1,2-dichloroethane). (A) Film gauge 0.04 mm; initial chlorine content 21%. Reaction at 24°, with 0.79M ferrocene. (B) Film gauge 0.10 mm; initial chlorine content 8.25%. Reaction at 50°, with 1.86M ferrocene.

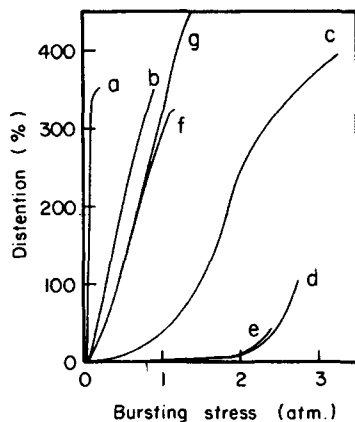


Fig. 2. Bursting stress-strain curves of polymer films (gauge 0.04 mm). (a) *cis*-polybutadiene (Taktene-1200); (b), (c), (d) solution-substituted polybutadienes containing 19.5, 32.2, and 34.0% ferrocene, respectively; (e) polyethylene (Ipethene 112); (f) solution-substituted polyethylene containing 34% ferrocene and 5.1% chlorine; (g) same as (f) for 9.4% ferrocene (initial chlorine content 40%).

by destruction of crystallinity during substitution. In the case of polybutadiene however, substitution leads to increased hardness. Thus, the initial slope to the distention axis of curve d, representing a substituted polybutadiene (34% ferrocene) is larger by some two orders of magnitude than that of Taktene-1200 (curve a). The glass transition temperatures were also found to increase considerably with the extent of ferrocenylation.⁸ The different mechanical behavior of the polymers represented by curves c and d is in good agreement with their glass transition temperatures -16° and $+16^{\circ}$, respectively. This dissimilarity cannot be explained in terms of ferrocene content, since the difference (32.2% and 34% ferrocene, respectively) is rather small. It has previously been postulated⁸ that during an advanced stage of the reaction, ferrocenylation may be accompanied by intramolecular ring formation between adjacent butene segments. The formation of cyclic structures along its backbone may restrict

TABLE II
Ferrocenylation of Chlorinated Polyethylene Films^a

Substrate		Treated film		
Film gauge (mm)	Chlorine content (%)	Ferrocene (%)	Mechanical properties	
			Residual bursting strength (%)	Residual distention (%)
0.040	7.3	3.6	102	93
0.040	21.0	4.1	104	88
0.040	27.8	7.4	95	95
0.100	5.5	2.6	98	107
0.100	16.7	4.2	92	107
0.100	22.6	4.4	80	100

^a Ferrocenylation carried out at 24° , during 80 sec, in 1,2-dichloroethane solution of ferrocene (0.79 M) and AlCl_3 (0.36 M).

considerably the mobility of the polymer molecule, resulting in higher T_g . Hence, it is possible that the much smaller distention in curve d, as compared with that in curve c, was the consequence of more extensive cyclization, rather than of the slightly higher ferrocene content.

The chemical transformations of the polymers during ageing were studied spectrophotometrically. Spectra of a ruthenocene-substituted polyethylene film, recorded after various exposure periods, are presented in Figure 3. The infrared spectrum [Fig. 3(A)] of the original film displayed characteristic features of the ruthenocene substituent⁷ (peaks at about 1100, 1000, and 810 cm^{-1}), the other main absorption bands belonging to the chlorinated polyethylene substrate.¹⁵ The oxidation of the polymer was indicated by the appearance of a "background depression" between 800 and 1400 cm^{-1} (ref. 16) and by increasing carbonyl¹⁷ and hydroperoxide¹⁸ bands between 1675 and 1800 cm^{-1} and 3300 and 3600 cm^{-1} , respectively. The depression in the 1500–1700 cm^{-1} region may be attributed to the formation of ethylenic unsaturation along the chain.¹⁹ A number of small peaks in the spectrum of the original film, located in regions characteristic to hydroxyl, carbonyl, and vinylene groups show that some degradation had already occurred during and/or following the substitution process, probably as a result of dehydrohalogenation.⁹

The hydroxyl, carbonyl, and vinylene bands were found to increase with the time of exposure, irrespective of substrate or method of substitution. Moreover, the position of the bands was the same for films exposed to sunlamp or to outdoor conditions.

Another common feature of the metallocene-containing polymers tested was the gradual darkening of their color when exposed to artificial or solar radiation, as exemplified in Figure 3(B). In this case, the originally colorless film turned greenish yellow after 210 hr of accelerated weathering. The color of ferrocenylated films was observed to change from yellowish to orange and on prolonged exposure even to reddish or tan. This tanning phenomenon was observed with all the polymetalloenes investigated and it appeared to be particularly dramatic with ferrocenylated polymers containing a substantial amount of halogen, as in the cases illustrated in Figures 4 and 5. Though in the case of halogen-containing polymetalloenes photolytic oxidation through a metallocene-halocarbon charge transfer complex²⁰ might be assumed, a different explanation is needed for the tanning of halogen-free polymers.

Whereas polymers containing both metallocene and halogen underwent color

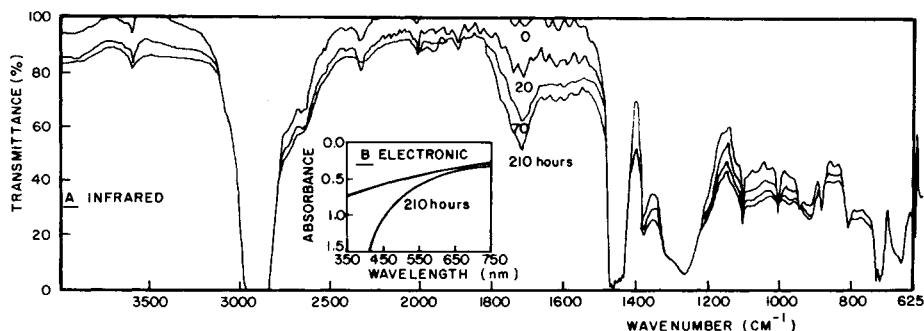


Fig. 3. Infrared (A) and electronic spectra (B) of ruthenocene-substituted polyethylene film (gauge 0.10 mm, 3.4% ruthenocene) recorded at various stages of accelerated weathering.

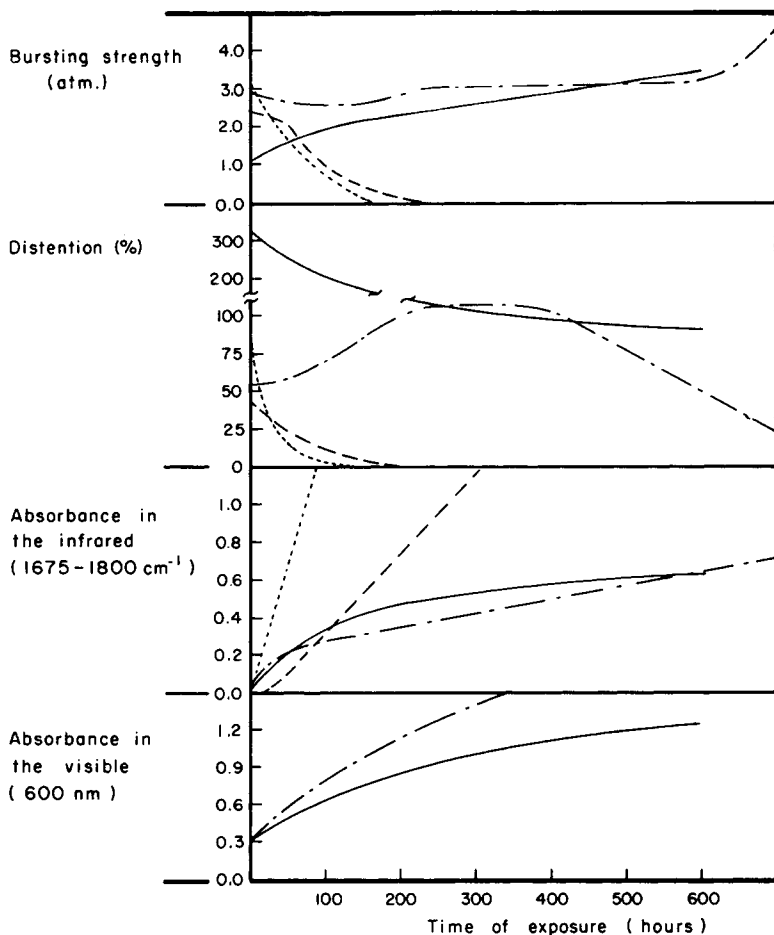


Fig. 4. Effects of accelerated weathering on polyethylene and substituted polyethylene films (gauge 0.04 mm). (---) polyethylene, (-·-) surface-chlorinated polyethylene (27.8% chlorine), (—) solution-ferrocenylated polyethylene (34% ferrocene, 5% chlorine), (- - -) surface-ferrocenylated polyethylene (8% ferrocene, 25% chlorine).

change even when irradiated in an inert atmosphere, ferrocenylated polybutadienes did not tan unless oxygen was present, indicating that tanning was connected with some oxidative process. Moreover, the fact that by treating a tanned polybutadiene-ferrocene film with alkaline solution the original yellow color returned gradually, suggested that the darker color had been caused by oxidation of ferrocene moieties to ferricenium ions. It was also observed that polybutadiene did not need to be chemically bound to the metallocene in order to get tanned: the same result could be obtained by exposing a solution of ferrocene in the respective polymer to ultraviolet light. Thus, a solution of 20% *n*-butylferrocene in a liquid oligobutadiene (Lithene QL) turned reddish upon irradiation whereas no color change occurred with *n*-butylferrocene dissolved in paraffin oil. On the other hand, when 0.1% tert-butylhydroperoxide was added to the paraffin solution and heated to 160°, the peculiar reddish color appeared instantly. All these observations seemed to imply that tanning was in fact the result of a thermal reaction between metallocene and hydroperoxides originating from the photooxidation of unsaturated chain units in the polymer. If that is

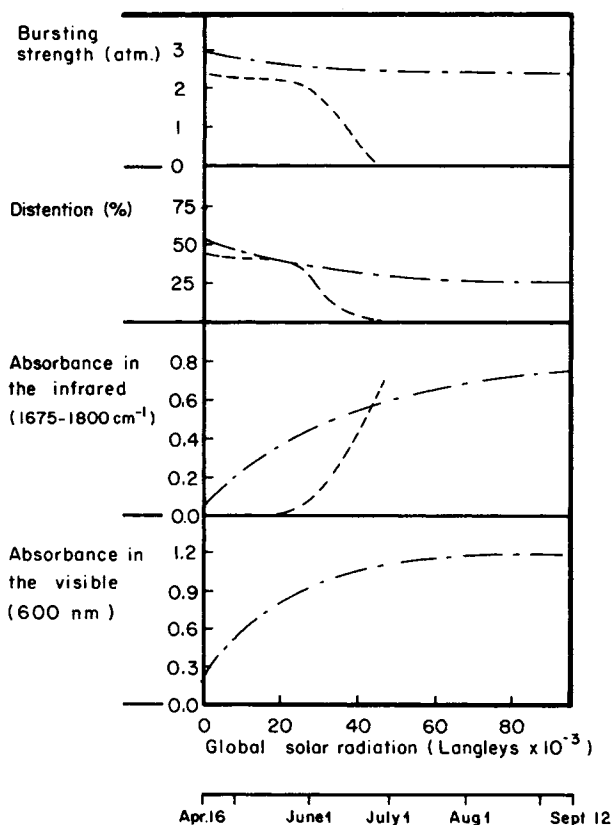


Fig. 5. Effect of outdoor weathering (Haifa, 1973) on 0.04-mm thick films of polyethylene (---) and surface-ferrocenylated polyethylene (8% ferrocene, 25% chlorine) (---).

the case, to minimize tanning, either halogen-free saturated polymers should be prepared, or the metallocene moiety should be made less susceptible to oxidation, e.g., by postacylation.²¹

The carbonyl absorbance curves in Figures 4 and 5 show that in contrast with polyethylene, which exhibits an induction period,¹⁸ the oxidation of ferrocene-substituted polymers is fast at the beginning, but it soon slows down to rates several times lower than that of polyethylene. On the other hand the chlorinated polyethylene, which served as substrate for ferrocenylation, was oxidized some three times faster than unsubstituted polyethylene (Fig. 4). Results of the mechanical testing of films, withdrawn after different weathering periods, are presented in the upper two diagrams of Figures 4 and 5. The useful lifetime of a polymer has been defined as the ageing period required to reduce the material's ultimate elongation to one third of its initial value.²² From this definition, the lives of the solution- and surface-ferrocenylated films represented in Figure 4, may be considered fourfold and tenfold longer, respectively, than that of unsubstituted polyethylene. In Figure 5 the distention of the same surface-ferrocenylated film was still 50% of the initial value after receiving 90,000 Langleys, whereas the lifetime of polyethylene—expressed in terms of global solar radiation—was 32,000 Langleys.

In order to study the performance of metallocene polymers as UV barriers,

polyethylene films—serving as actinometers²³—were placed below the exposed 0.04 mm thick ferrocenylated polymer films. By extrapolating the time of exposure required to reach a carbonyl absorbance of 0.4 (corresponding roughly to $\frac{2}{3}$ reduction of the elongation at break), the useful life of polyethylene films could be anticipated to be up to 70 times longer than that of unprotected polyethylene.

Ferrocenylated polybutadienes were found to be oxidized and consequently to deteriorate faster than the corresponding ferrocenylated polyethylene. In a typical example, the polymer represented by curve c in Figure 2 reached within 100 hr of accelerated weathering a carbonyl IR absorption as high as 0.7, whereas its distention was down from about 400% to 30%. In the same time, however, the bursting strength remains at its initial level of about 3 atm. Similarly in the case of substituted polyethylenes, while the distention appears to decline after prolonged exposure, the bursting strength either remains practically unchanged (Fig. 5) or even increases (Fig. 4). A possible explanation may be that in the photodegradation of metallocene-substituted hydrocarbon-chain polymers considerable crosslinking occurs, which balances or even outweighs the effect of fragmentation. By analogy with polystyrene,²⁴ crosslinking may be assumed to take place through radicals formed by elimination of hydrogen from tertiary chain carbons, α to the metallocene moiety.

Preliminary experiments in our laboratory with poly(vinyl fluoride) and chloromethylated polystyrene indicate the feasibility of similar metallocene modifications.

The potential usefulness of metallocene modified polymers is under further investigation.

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