Photomechanical effects in polymers containing 6'-nitro-1,3,3-trimethyl-spiro-(2'H-1'-benzopyran-2,2'-indoline)

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The photomechanical response of polystyrene and polymethyl methacrylate containing 6'-1,3,3-trimethyl-spiro-(2H-1-benzopyran-2,2' indoline), were investigated. The effects of the concentrations of the photochrome and of the initial stress were studied and the rates of the dark relaxation responses compared with the rates of decolouration of the photochrome.

Keywords Photochromism; photomechanical effects; photoresponsive polymer; polystyrene; polymethylmethacrylate; spirobenzopyran

INTRODUCTION

The first synthesis of a photomechanical polymeric system was that of Lovrien[1] who designed two systems for controlling polymer configuration by light. He studied these systems in solution and since the viscosity of a polymer system is in part a reflection of polymer configuration these reversible photomechanical effects were reported as 'photoviscosity effects'. These effects were not trivial ones such as those brought about by the simple heating of the systems due to the adsorption of light.

Photomechanical effects in gels provides a link between photoviscosity effects observed by Lovrien and co-workers and the discovery of photomechanical effects in the solid state. Van der Veen and Prins[2] predicted that the effect which, in solution, gave rise to viscosity changes, will, in gels, result in volume changes. The photomechanical properties were discovered by irradiating membranes of poly(hydroxy/ethyl methacrylate) which had been swollen in an aqueous solution of Chrysophenine G. The system was found to contract on irradiation while length recovery occurred under dark conditions. The system could be cycled many times. From their results Van der Veen and Prins postulated a model for photomechanical energy conversion. They suggested that the polymer swelled as a result of the binding process with Chrysophenine, that is, the dye disturbed some pre-existing order within the polymer. Upon irradiation, the dye underwent isomerization and the interaction between dye and polymer lessened. In this way the perturbing effect of the dye was undone and it was the ability of the polymer to undergo co-operative rearrangement that led to amplification of the effect of *cis–trans* isomerization of the dye, which produced a gross photomechanical effect.

The first report of photomechanical effects in the solid state was that of Husy, Merian and Schetty in 1969[3], who observed that an acetate ribbon dyed with an azo dye contracted when exposed to sunlight. On storage in the dark the sample regained its original length. Ribbons dyed with dyes which did not contain an isomerizable group, did not contract. Their conclusion therefore was that this photomechanical effect was due to the *cis–trans* rearrangement of the azo dye. In 1970 Agolini and Gay[4] reported both photo- and thermo-contractile effects with certain azo aromatic polymers. Again the contractile properties were attributed to the presence of azo-linkages which could undergo *trans*→*cis* isomerization.

More recently Smets and de Blauwe[5] studied the mechanical properties of certain polyethyl acrylates containing spirobenzopyran crosslinks. On irradiation, a contraction of more than 2% occurred in isothermal conditions, while in the dark, length recovery took place; the process was reversible.

The present report describes the observation and measurement of photomechanical responses in polymeric systems in which a photochrome, 6'-nitro-1,3,3,-trimethyl spiro(2'H-1'-benzopryan-2,2'-indoline) has been incorporated in the form of a simple solid solution. The polymers used in this investigation were polymethyl methacrylate and polystyrene.

EXPERIMENTAL PROCEDURE

Sample preparation

Films of polystyrene and polymethyl methacrylate containing 1, 3, 5, 10 and 20% w/w 6'-nitro 1,3,3-trimethyl-spiro- (2'H-1'-benzopyran 2,2' indoline) were prepared by first dissolving the polymer and photochrome in xylene and then casting on mercury. The films when 'dry' were removed and placed in a vacuum oven for 48 h to ensure complete removal of solvent. The entire procedure was carried out under safe light conditions.

Measurement of photomechanical response

An Instron Tensile Tester was used to carry out constant length experiments in which strips of photochromic film, placed under stress, were exposed to ultra-violet radiation and then allowed to recover in complete darkness; the process being reversible. Stress changes with time were recorded for each light–dark cycle until a reproducible result was achieved.

Results were obtained for different concentrations of photochrome, each being subjected to a different initial stress. Again the entire experimental procedure was carried out under 'safe-light' conditions, the 'safe-light' providing only sufficient illunination to permit manipulation of the instrument controls. Precautions were taken to avoid thermal effects from the u.v. source.

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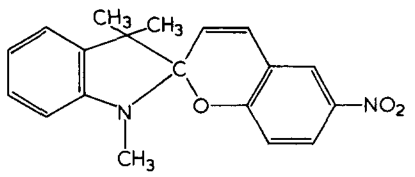
RESULTS AND DISCUSSION

6-Nitro-1,3,3,-trimethylspiro-(2′H-1′-benzopyran-2,2′-indoline) is a photochromic spiropyran with a structure as shown (I).



The open ring merocyanine form is characterized by a very strong absorption in the visible range of the spectrum. What is not apparent from this two dimensional diagram is that the pyran section and the indoline section lie in planes which are orientated at an angle of 90° to each other giving rise to a comparatively bulky molecule. The merocyanine molecule however has a planar structure and therefore the photochromic process results in significant changes in the molecular dimensions. It was therefore expected that incorporation of this molecule within a polymer matrix would produce a photomechanical effect.

Both polymer/photochrome systems exhibited a photomechanical effect which was small in terms of change in length but which could be easily quantified in terms of change in stress with constant length experiments.

Figure 1 shows an idealized response of these polymer systems in a light–dark cycle. On irradiation, the initial stress applied to the sample decreases indicating an expansion of the sample, while in the dark, length recovery takes place by a subsequent contraction indicated by an increase in stress.

It was found that initially the dark recovery was less than the expansion on irradiation but after a few light/dark cycles the process became entirely reversible. This phenomen has been termed 'photoinduced creep' since the result is a permanent extension of the sample.

As controls, samples of pure polystyrene and polymethyl methacrylate were subjected to the same light/dark cycles. No significant photomechanical response was observed with either polymer.

Figure 2 shows the response of a sample of polystyrene containing 5% w/w photochrome in terms of change in stress against time for the irradiation part of the cycle. The curves show the results of varying the initial stress applied to the sample.

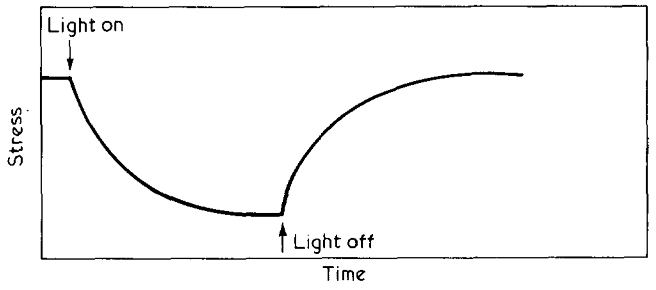


Figure 1 Idealized response for a photoresponsive polymer in a light–dark cycle

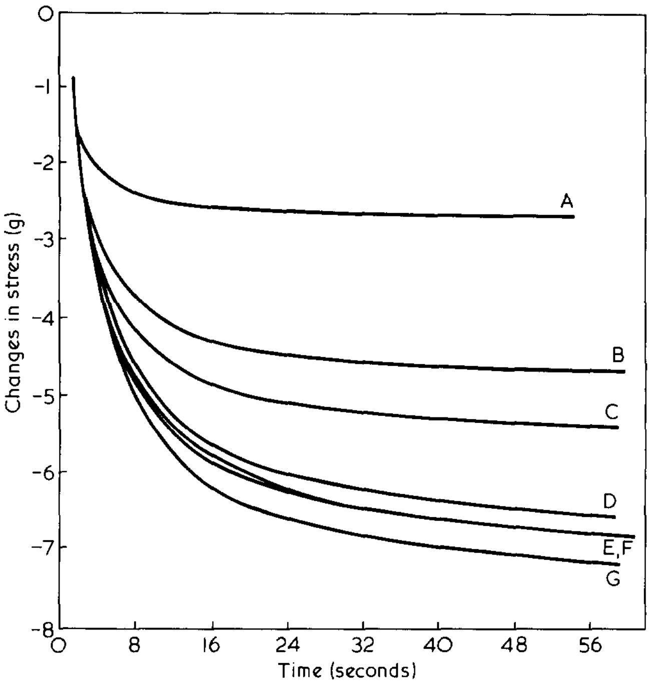


Figure 2 Dependence of photomechanical response on initial stress. Polystyrene film and 5% photochrome. Initial stress (A) 4g, (B) 7g, (C) 9g, (D) 14g, (E) 19g, (F) 30g, (G) 45g

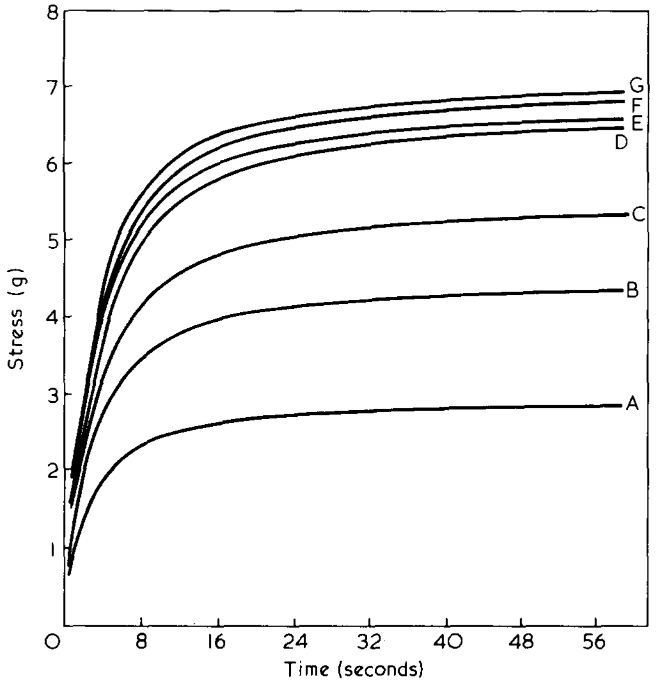


Figure 3 Dependence of dark recovery on initial stress. Polystyrene film and 5% photochrome. Initial stress (A) 4g, (B) 7g, (C) 9g, (D) 14g, (E) 19g, (F) 30g, (G) 45g

Figure 3 shows the response of the same sample of polystyrene after irradiation is terminated, i.e. the dark recovery. Again the curves shown correspond to recoveries from the extended state for varying initial stresses. The effect of increasing initial stress is more clearly seen in *Figure 4*.

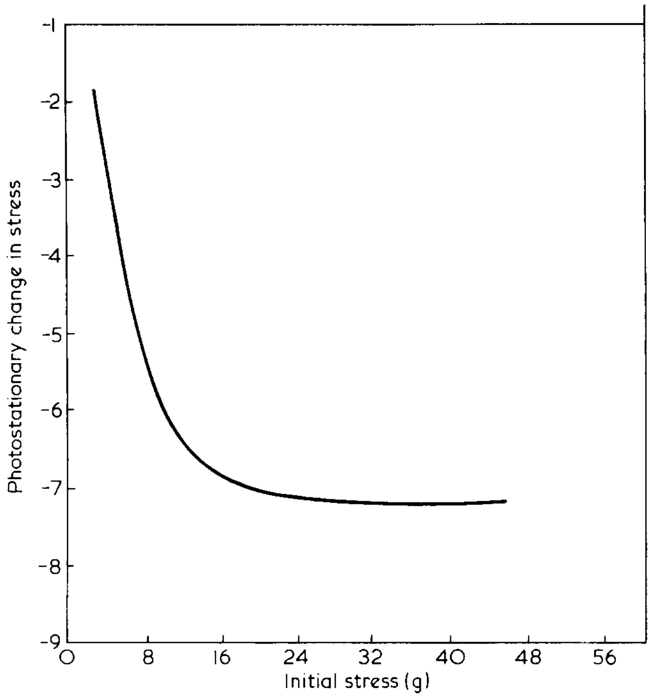


Figure 4 Dependence of photomechanical response on initial stress. Polystyrene and 5% photochrome

The dependence of the photomechanical effect on the concentration of photoresponsive compound is illustrated in *Figure 5*.

For polystyrene a maximum photomechanical effect is achieved with a concentration of approximately 5% (w/w) photochrome. Below this level the photomechanical effect increases rapidly with increasing concentration, while at concentrations above this level the photomechanical effect decreases slowly.

The fact that these polymeric systems exhibit a photomechanical response may be explained by consideration of the change in entropy involved in the photochromic process. The spiropyran molecule has a comparatively bulky structure when compared with the merocyanine structure, which is planar. If these molecules are to be dispersed monomolecularly throughout the polymer, then a certain amount of disturbance to the packing of the polymer chains must occur. The disturbance resulting from the presence of a spiro molecule will be greater than that resulting from a planar merocyanine molecule. Hence a conversion from the spiro structure to the planar merocyanine structure will result in an overall decrease in entropy of the system since the polymer molecules will be allowed to pack closer together. Therefore, in agreement with the theory put forward by Smets and De Blauwe[5], a reduction in entropy will result in an expansion of the system. In the dark there is a conversion back to the spiro structure which will increase the entropy of the system and result in a contraction of the sample.

However, unlike the systems investigated by Smets and De Blauwe, the photochromic process occurring during irradiation will not cause a change in entropy, but will allow an entropy change to take place. This explains the dependence of the photomechanical response on the initial stress applied to the sample. The entropy change will only take place under the influence of an external force, i.e. the stress applied to the sample. The maximum allowable entropy change will therefore only be achieved if an adequate stress is applied. Hence the dependence on the initial stress applied to the sample.

During the dark recovery, the conversion back to the spiro structure will cause a change in entropy. However, the apparent dependence on the stress applied stems from the fact that the entropy change occurring can only equal that already obtained from the irradiation part of the cycle which is stress dependent.

If it is assumed that the photomechanical effect is a result of isomerization of very many photochromic molecules, each producing a slight movement of neighbouring atoms, then the gross effect of expansion or contraction of the polymer sample must be brought about by co-operative re-arrangement of the polymer molecules. A possible explanation of the dependence of the response on photochrome concentrations is that at low concentrations the co-operative effect re-arrangement occurs unhindered. However, as the concentration rises above a certain value the interaction between polymer molecules becomes less due to the sheer bulk of the photochromic molecules and therefore the degree of co-operative re-arrangement becomes smaller. Consequently the photomechanical effect decreases as the photochrome concentration rises above this critical level.

The photomechanical response of the polymethyl methacrylate/photochrome system shows a similar dependence on initial stress and concentration of photochrome as the polystyrene/photochrome system, as shown in *Figures 6* and *7*. It would appear, therefore, that the assumptions made so far apply equally to the polymethyl methacrylate/photochrome system.

On comparison of the photomechanical effect with that obtained by Smets and De Blauwe, it is apparent that the effect obtained, when the photoresponsive unit is present as a component of a homogeneous mixture, is in the

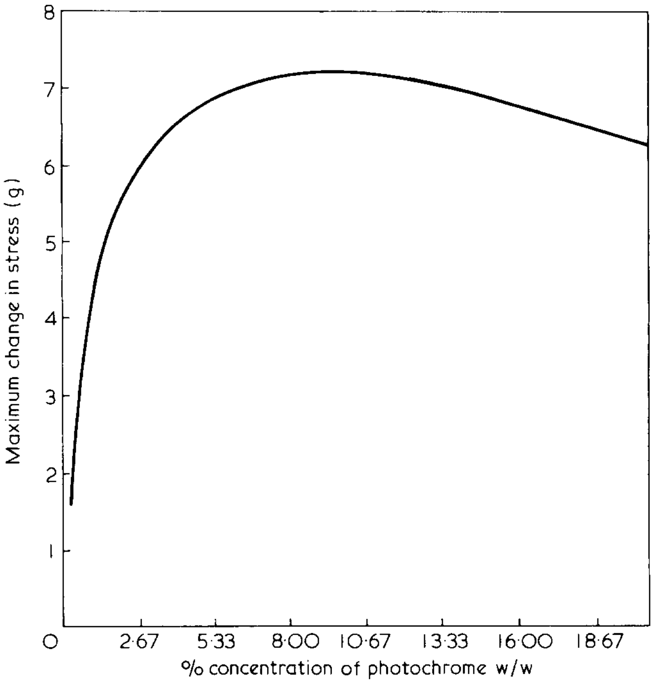


Figure 5 Dependence of the photomechanical effect in polystyrene on concentration of photochrome

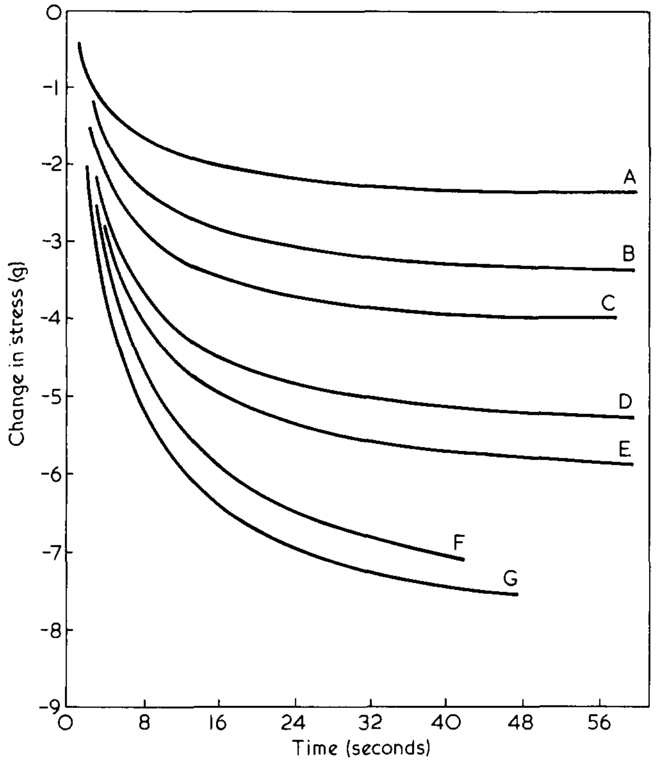


Figure 6 Dependence of photomechanical response on initial stress. Polymethyl methacrylate film +5% photochrome. Initial stress (A) 4g, (B) 7g, (C) 9g, (D) 14g, (E) 19g, (F) 30g, (G) 45g

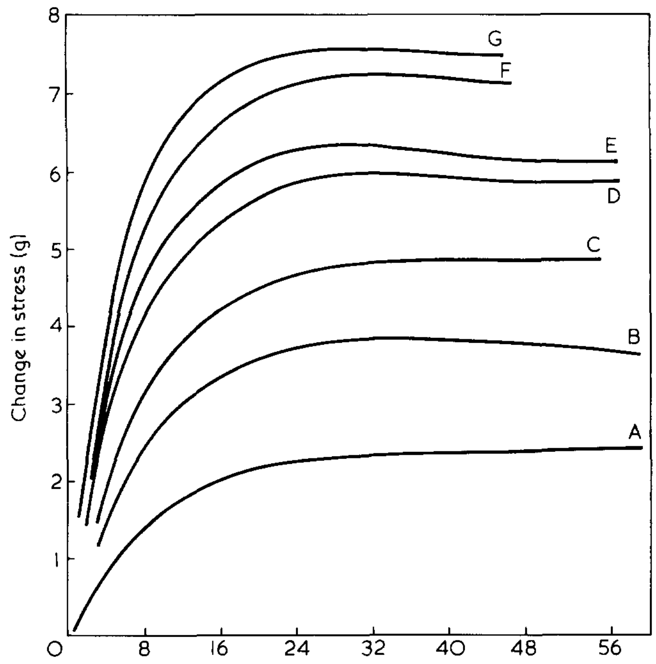


Figure 7 Dependence of dark recovery on initial stress. Polymethyl methacrylate +5% photochrome. Initial stress (A) 4g, (B) 7g, (C) 9g, (D) 14g, (E) 19g, (F) 30g, (G) 45g

opposite direction to that obtained when the unit is incorporated in the polymer structure. That is, on irradiation an extension as opposed to a contraction occurs. The speed with which the expansion or contraction takes place is also much faster than that observed with the crosslinked polyethyl acrylates. With the systems presently under investigation the photostationary state is achieved within seconds whereas the crosslinked copolymers took 7–8 min to reach this state[5].

If it is assumed that the photomechanical effect is a result of isomerization of the photochromic molecules, the rate of contraction or expansion should be similar to or slower than the rate of decolouration. The rate would be slower if, as suggested by Agolini and Gay[4], the visco-elastic properties of the sample were the rate governing factors in the mechanism. However, the photomechanical effect with the present system occurs more rapidly than the rate of decolouration of the photochrome which has a half life of ~20–30 min.

From *Figures 8* and *9* in the short term a number of fast decolouration rates and apparent, and within the time scale of the photomechanical effect of both polystyrene and polymethyl methacrylate systems, at least two distinct, fast, first order reaction rates can be observed. It is therefore suggested that the photomechanical effect is due to isomerization of only those molecules which are taking part in these initial fast reactions.

It is further suggested that these faster reaction rates are due to the isomerization of molecules which have been held in a strained state within a restricted location. This implies that the photomechanical response is a result of

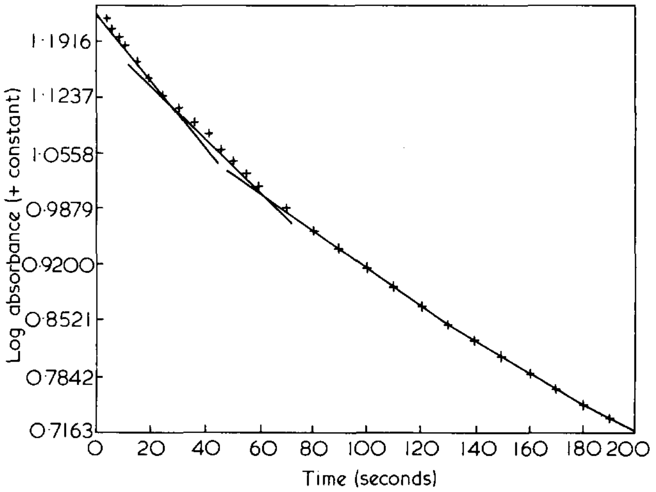


Figure 8 Short term fast decolouration rates for 5% photochrome in polystyrene

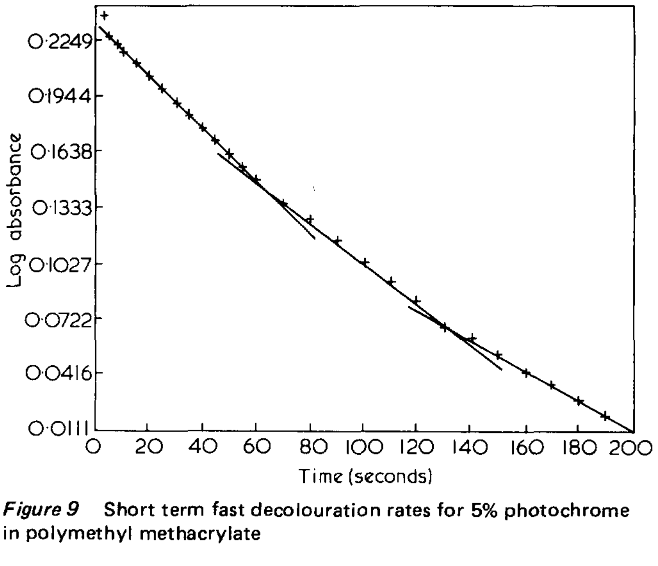


Figure 9 Short term fast decolouration rates for 5% photochrome in polymethyl methacrylate

isomerization of photochromic molecules within restricted locations and that these molecules are only a small fraction of the total concentration of photochromic compound present. The photomechanical response can therefore be thought of as being produced by molecules occupying certain 'sites' within the polymer matrix.

Further evidence in support of this hypothesis was obtained from a computer curve fitting exercise. This produced an equation which closely describes the photomechanical response occurring during dark recovery of the polystyrene system. This equation is:

$$\mathrm{Log}_e\,(\text{stress}) = K_\alpha\left(\frac{1}{\text{time}}\right) - K_\beta\left(\frac{1}{\text{time}}\right)^2 + K_\gamma$$

The lines drawn in *Figure 3* are described by the equation shown above. The constants calculated for each line are tabulated in *Table 1*.

The implication of this equation is that the curves obtained are the resultant of two opposing logarithmic functions. It is therefore suggested that the observed contraction with polystyrene is the net result of a larger contraction opposed by a smaller and more rapid expansion.

Table 1 5% w/w Photochrome in polystyrene dark recovery

Initial stress (grams)	K_α	K_β	K_γ
4	−1.43	−0.572	1.49
7	−1.63	−0.815	1.92
9	−1.69	−0.845	2.14
14	−1.31	−0.786	2.62
19	−0.916	−0.549	2.92
30	−0.540	−0.324	3.66
45	−0.429	−0.257	3.78

REFERENCES

1 Lovrien, R. 'Light Control of Viscosity of Reversible Macromolecular Photoresponses', 148th Am. Chem. Soc. Meeting, (1964), Abstract

2 Van Der Veen, G. and Prins, W. *Nat. Phys. Sci.* 1971, **230**, 70; *ibid Photochem. Photobiol.* 1974, **19**, 191

3 Husy, H., Merian, E. and Schetty, G. *Text. Res. J.* 1969, **39**, 94

4 Agolini, F. and Gay, F. P. *Macromolecules* 1970, **3**, 349

5 Smets, G. and De Blauwe, F. *Pure Appl. Chem.* 1974, **39**, 225

Effect of additives and solvents on polymerization of styrene using $CuCl_2 + AlEt_2Cl$ catalyst system

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The effect of additives and solvents is reported on the rate of polymerization of styrene by the catalyst system ($CuCl_2 + AlEt_2Cl$). The electron donating additives triphenylphosphine, anisole and diphenyl ether decreases the rate but hydroquinone has no effect on the rate. Increasing dielectric constant of solvents decreases the percentage conversion but chlorinated hydrocarbons do not obey the trend.

Keywords Insertion; polymerization; styrene; additives; solvents; catalyst

INTRODUCTION

We have reported in our previous communications[1-3] the use of Ziegler–Natta catalyst systems with copper-chloride as a transition metal component. A detailed study of the effect of electron donors and solvents was reported for the system $CuCl_2 + AlEt_2Br$[2]. In this communication we present some observations made on $CuCl_2 + AlEt_2Cl$ catalyst system.

EXPERIMENTAL

Purification of monomer, solvent, additives and the polymerization procedure are the same as reported earlier[2].

The following reaction conditions were used: $[CuCl_2] = 0.01$ mol l^{-1} [Al]:[Cu] = 1.6, ageing time = 4.0 h, styrene = 1.743 mol l^{-1}, total volume = 25.0 ml, temperature = 30°C.

RESULTS AND DISCUSSION

Effect of various additives and solvents are summarized in *Tables 1* and *2*.

It can be seen that with increasing amount of triphenylphosphine (PPh_3) the catalyst activity decreases. This has been already observed in case of

Table 1 Effect of additives on system $CuCl_2/AlEt_2Cl$ for styrene polymerization

Additive	[Additive] mol l^{-1}	Rate (R_p) mol l^{-1}	Reaction time (hours)
–	–	37.57×10^{-5}	00.5
–	–	1.08×10^{-5}	40.0
PPh_3	2×10^{-3}	2.95×10^{-5}	08.0
	4×10^{-3}	1.30×10^{-5}	08.0
	6×10^{-3}	1.43×10^{-5}	08.0
	8×10^{-3}	1.91×10^{-5}	08.0
	100×10^{-3}	0.04×10^{-5}	08.0
Anisole	18×10^{-3}	4.599×10^{-6}	30.0
	72×10^{-3}	0.498×10^{-6}	30.0
	144×10^{-3}	1.680×10^{-6}	30.00
	180×10^{-3}	1.460×10^{-6}	30.0
DPE	12×10^{-3}	1.43×10^{-5}	40.0
	50×10^{-3}	1.38×10^{-5}	40.0
	99×10^{-3}	1.25×10^{-5}	40.0
	120×10^{-3}	1.45×10^{-5}	40.0
Hydroquinone	6×10^{-4}	38.5×10^{-5}	00.5

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