

Flexible poly(vinyl chloride) sheets: 1. Interrelations between ultra-violet irradiation and plasticizer migration into alcohols

C. D. Papaspyrides

Laboratory of Special Chemical Technology, Department of Chemical Engineering,
National Technical University of Athens, 42 Patission Street, Athens 106 82, Greece
(Received 13 January 1986; revised 21 April 1986)

Ultra-violet (u.v.) irradiation of poly(vinyl chloride) (PVC) sheets is a well known technique for inducing surface crosslinking in order to prevent plasticizer migration phenomena. Accordingly, for varying u.v. irradiation doses, long-term migration data obtained by radioactivity measurements are presented for the systems PVC/labelled dioctyl phthalate (DOP)/methanol, ethanol, n-propanol and n-butanol. Even at the higher doses examined, migration was found to be only moderately hindered; primary kinetics studies also yielded similar results to those already established for untreated material. This behaviour was attributed mainly to counterdiffusion processes resulting in progressive failure of the protective surface layer developed during irradiation.

(Keywords: poly(vinyl chloride); dioctyl phthalate; alcohols; ultra-violet irradiation; plasticizer migration)

INTRODUCTION

Plasticizer migration from poly(vinyl chloride) remains a critical problem due to the high consumption of this polymer in flexible form. In the literature, great emphasis is given to solid/liquid systems simulating common food packaging and medical applications. Possible factors affecting the phenomenon, such as nature and concentration of plasticizer, plasticization process, surrounding medium and conditions of test, have been extensively studied¹⁻¹⁴, but research is also focused on constructing a model system capable of describing migration in precise terms^{7-11,15}.

In conjunction with this research activity, many investigators have concentrated their efforts on reducing or completely preventing migration. The simplest technique proposed consists of placing a contact layer, such as absorbing paper or metal foil, on the surface of plasticized PVC films^{16,17}. Nevertheless, numerous studies also include coating with polyurethanes¹⁸⁻²⁰, polyacrylates²¹⁻²³, polyesters^{19,24} and polyamides^{25,26}. In addition, efforts have been made to modify the structure of the packaging material itself by either crosslinking or incorporation of bulky substituents, i.e. to restrain the mobility of the system species⁸.

Incorporation of bulky substituents in PVC has been effected through copolymerization with monomers, such as vinyl acetate and vinyl propionate²⁷, or by adding suitably selected additives, such as siloxanes^{28,29}. On the other hand, bulk crosslinking may be induced chemically, e.g. by processing with peroxides³⁰, or by radiation in the presence^{31,32} or absence of multifunctional monomers. In the latter case, use of gamma rays³³, u.v. light³⁴⁻³⁶ as well as plasma treatment³⁷⁻⁴¹ has been widely applied for preventing migration while, depending on the choice of the radiation source, the penetration depth is varied.

In this paper the transfer of labelled DOP from irradiated PVC sheets into alcohols, namely methanol, ethanol (96%), n-propanol or n-butanol, is examined. In particular, the influence of moderate treatment with u.v. light is considered, until equilibrium, for different irradiation doses. An attempt to test the data obtained against typical Fickian behaviour and further to correlate results with alcohol countereffects is also included.

EXPERIMENTAL

Synthesis of ¹⁴C-labelled dioctyl phthalate

This is as previously described^{2,3}.

Plasticization

A suspension of PVC of *K* value 65 was blended, at 80°C, with the calculated amounts of labelled plasticizer and Ba-Cd stabilizer corresponding to levels of 50 and 3 phr respectively. The dry blend was plasticized for 7 min in a Brabender Plasticorder at 170°C and 30 r.p.m. The plasticized mass obtained was then hot pressed to form a sheet of about 2.5 mm thickness. From this sheet, specimens of 20 × 50 mm were cut.

Ultra-violet irradiation

Both sides of the specimens were irradiated with u.v. light (emitted mainly at 254 nm) from a 15 W GE germicidal lamp placed at a distance of 10 cm at room temperature. Gel fractions of the irradiated material were determined by extracting with tetrahydrofuran (THF) for 24 h and vacuum drying at 70°C overnight⁴². The volume of solvent used for extraction was greater than 1500 ml g⁻¹ of polymer.

Immersion

Each of the specimens was immersed in 250 ml liquid contained in a glass-stoppered Erlenmeyer flask of 300 ml. All tests were made in duplicate and the flasks were kept in an oven fixed at $35 \pm 1^\circ\text{C}$. To monitor weight changes, the specimens were removed from the liquid environment, wiped gently with a tissue and immediately weighed.

Radioactivity measurements

The radioactivity (R_t , counts per millilitre per minute) of the liquid medium represents the concentration of the plasticizer migrated at immersion time t . Multiplied by the volume of the liquid environment (250 ml) and divided by the radioactivity of the plasticizer employed ($R_0 = 3011 \pm 12$ counts per milligram per minute), the overall DOP quantity migrated (Q_t , mg) from the specimen immersed is calculated.

The detailed procedure for measuring radioactivity has been described elsewhere²⁻⁵.

RESULTS AND DISCUSSION

Effect of irradiation time on gel content

It is well known that u.v.-induced crosslinking of PVC is also accompanied by degradation effects⁴²⁻⁴⁴. Both actions are largely dependent on radiation dose, i.e. irradiation time, and therefore the need arises to evaluate their interrelations. Crosslinking confers insolubility while degradation reactions become primarily evident by discoloration. Accordingly, in *Figure 1* is shown the relation found between gel content and irradiation time under our experimental conditions. The curve is linear for irradiations up to about 14 days and then appears to become concave to the abscissa. On the other hand, beyond this limit discoloration of the specimen surface becomes quite evident and therefore it seemed worthwhile to confine irradiation experiments below 14 days.

Migration behaviour of irradiated material

Specimens irradiated for 3, 7 and 13 days together with non-treated ones were used to study the transfer of plasticizer into the alcohols considered. In *Table 1* equilibrium values of plasticizer migrated are given, expressed as weight percentage of the amount of plasticizer initially contained in the material. In

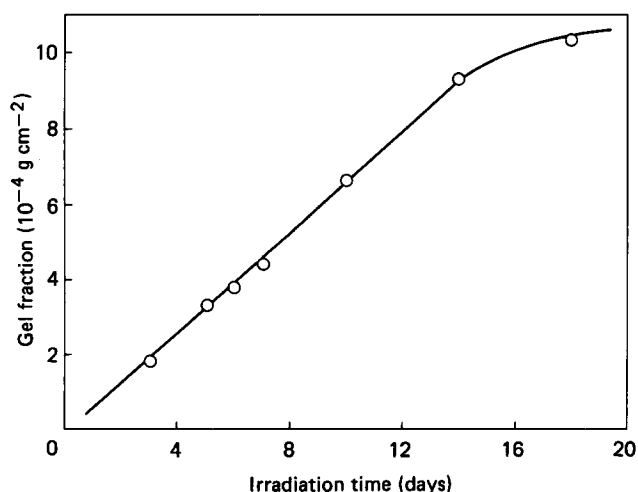


Figure 1 Relationship between gel content and irradiation time

Table 1 Equilibrium values of plasticizer migrated expressed as weight percentage of the initial quantity contained

Liquid environment	Irradiation time (days)			
	0	3	7	13
Methanol	86	84	76	70
Ethanol (96%)	86	85	77	74
n-Propanol	100	99	94	92
n-Butanol	99	99	97	95

Table 2 Equilibrium values of alcohol counterdiffused (expressed on initial weight percentage basis)

Liquid environment	Irradiation time (days)			
	0	3	7	13
Methanol	8.2	7.8	7.3	6.1
Ethanol (96%)	9.2	8.9	8.3	8.0
n-Propanol	10.5	10.3	9.7	9.5
n-Butanol	9.8	9.6	9.1	9.0

agreement with previous studies^{2,4} the higher molecular weight alcohols favour greater migration levels. Indeed, data concerning the non-treated specimens confirm that for propanol and butanol, in contrast with the lower alcohols, all of the plasticizer eventually migrates. On the other hand, it is clear that the equilibrium migration level decreases with irradiation time while very little difference appears between the irradiation levels of 0 and 3 days as well as between 7 and 13. Nevertheless, these results indicate clearly that the u.v. treatment adopted has not proved very effective in preventing migration.

Counterdiffusion phenomena

It is well known that in solid/liquid systems plasticizer migration is usually accompanied by diffusion of the liquid into the plastic^{1-6,8-11,15}. Furthermore, the case of PVC/DOP/alcohols is characterized by separation of alcohol counterdiffused in a second phase within the plastic mass⁴. In fact, this phenomenon was also observed in our specimens after immersion, while the amount of alcohol sorbed at equilibrium was found, by weight measurements⁸, to be related to irradiation time in a manner similar to that encountered in migration (*Table 2*).

Careful examination of specimens irradiated and then immersed revealed two different modes of surface appearance: specimens placed in methanol and ethanol were characterized even from the beginning of the immersion experiment by distinct surface pitting; on the other hand, immersion in the higher alcohols was marked, mainly during the latter stages, by partial or total detachment of a top surface layer (*Figure 2*). The latter, when collected, dried and treated with THF under reflux, remained completely insoluble and thus obviously comprised the crosslinked tissue developed during irradiation. In fact, it is well known that for PVC any u.v.-induced phenomena are confined to a thin surface layer approximately 0.2 mm thick⁴³⁻⁴⁶.

The above observations lead to a quite satisfactory explanation of the resulting behaviour either from a migration or counterdiffusion point of view. In fact, u.v. treatment is effective when the crosslinked layer developed is 'strong' enough to resist penetration, except

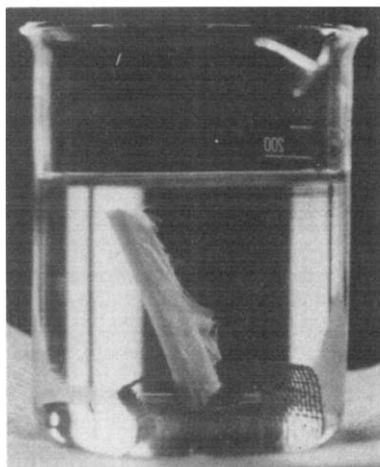


Figure 2 Detached surface layer from a specimen after immersion in n-butanol for 74 days (irradiation time 13 days)

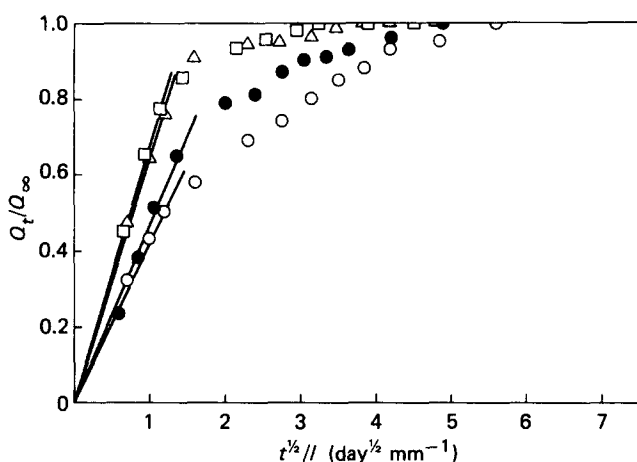


Figure 3 Relationship between Q_t/Q_∞ and $t^{1/2}/l$ for non-irradiated specimens: (○), methanol; (●), ethanol; (□), n-propanol; (△), n-butanol

from inside, by the liquid environment. Larger volume molecules eventually succeed in detaching the crosslinked tissue, but this is not the case with the smaller ones which nevertheless from the beginning reduce its uniformity by pitting. Subsequently, plasticizer migration is considerably less obstructed and equilibrium states as in Table 1 are established.

Plasticizer migration kinetics

Plasticizer migration is a typical desorption process. In an attempt to examine kinetics, Fickian behaviour with constant diffusion coefficient was first considered, described for a plane sheet by the following equation⁴⁷:

$$\frac{Q_t}{Q_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{\exp\{-(2n+1)\pi/l\}^2 Dt\}}{(2n+1)^2} \quad (1)$$

where Q_∞ represents the amount desorbed at infinite time, l the thickness of the sheet and D the diffusion coefficient. Nevertheless, the well known approximation for short times:

$$Q_t/Q_\infty = (4/l)(Dt/\pi)^{1/2} \quad (2)$$

is also useful. A plot of Q_t/Q_∞ against $4(t/\pi l^2)^{1/2}$ is initially linear and has a slope of $D^{1/2}$.

In a previous paper from our laboratory¹⁰ the conformity of the migration data, for the untreated

specimens, to Fickian behaviour has already been tested. While the ethanol case had not been considered, in all cases short-term data were found to be consistent with equation (2). On the other hand, tests of Q_t/Q_∞ against t definitely failed to provide a linear relationship, which corresponds to segmental relaxation control, a type of transport process also well known as the 'case II' diffusion model^{47,48}.

The situation does not change appreciably after u.v. treatment. The data are not in agreement with case II behaviour and the short-term Fickian relationship was again obeyed independently of alcohol nature and irradiation dose. In Figures 3–6 the reduced desorption curves of Q_t/Q_∞ versus $t^{1/2}/l$ are shown, either for untreated (now ethanol has been included) or treated specimens. The linearity of the initial portion of the curves is evident, extending up to values of Q_t/Q_∞ varying between 0.5 and 0.8. In fact, in all cases correlation coefficients—by the least-squares method—coincide with unity. Table 3 provides comparative values of the diffusion coefficient, of course referred to the initial stages of the immersion process. Clearly, the diffusion coefficient decreases with irradiation dose and the effect on the time required for the establishment of the equilibrium also seems similar. Furthermore, it should be noted that there is a small difference effected in the value of D for methanol, in which pitting can be distinguished from the beginning. On the contrary in the other media, where

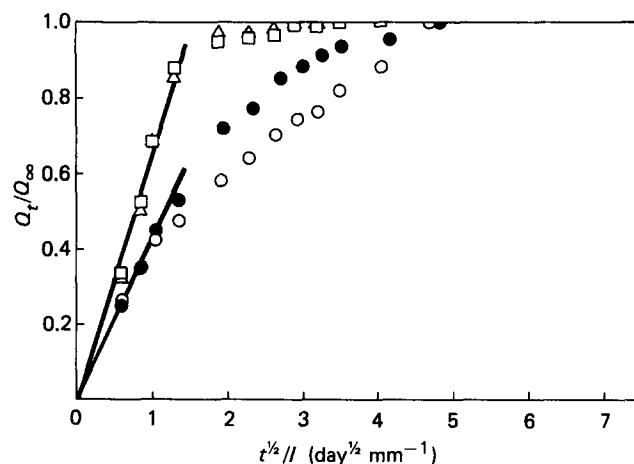


Figure 4 Relationship between Q_t/Q_∞ and $t^{1/2}/l$ for irradiated specimens (3 days): (○), methanol; (●), ethanol; (□), n-propanol; (△), n-butanol

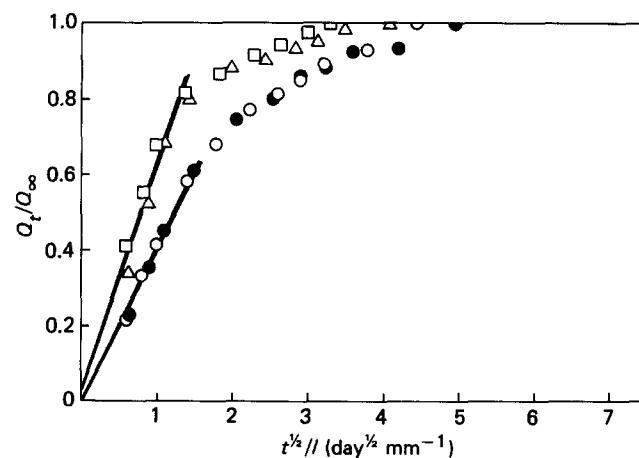


Figure 5 Relationship between Q_t/Q_∞ and $t^{1/2}/l$ for irradiated specimens (7 days): (○), methanol; (●), ethanol; (□), n-propanol; (△), n-butanol

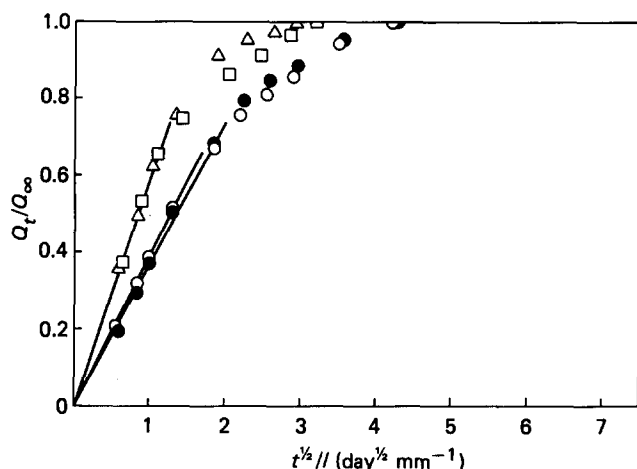


Figure 6 Relationship between Q_t/Q_∞ and $t^{1/2}/l$ for irradiated specimens (13 days): (○), methanol; (●), ethanol; (□), n-propanol; (△), n-butanol

Table 3 Diffusion coefficient values ($\text{cm}^2 \text{s}^{-1}$) according to Q_t/Q_∞ versus $t^{1/2}/l$ linear correlation

Liquid environment	Irradiation time (days)			
	0	3	7	13
Methanol	4.0×10^{-9}	3.9×10^{-9}	3.8×10^{-9}	3.8×10^{-9}
Ethanol (96%)	5.2×10^{-9}	4.1×10^{-9}	3.6×10^{-9}	3.1×10^{-9}
n-Propanol	1.0×10^{-8}	9.7×10^{-9}	8.6×10^{-9}	7.6×10^{-9}
n-Butanol	9.5×10^{-9}	9.5×10^{-9}	8.5×10^{-9}	7.6×10^{-9}

pitting phenomena are limited, differences arise due mainly to the time required for the observed detachment of the crosslinked surface tissue.

The kinetics analysis stated above is undoubtedly quite simplified, still ignoring for instance boundary layer phenomena in the liquid phase¹¹. Nevertheless, the picture obtained is consistent with the observations revealing the partial failure of the protective top layer, which has been mainly attributed to alcohol countereffects. If this is correct, then use of non-penetrating liquids³ may lead to better prevention so that current research is now focused on this point while further considering, also on mechanical properties, the effect of greater irradiation doses.

ACKNOWLEDGEMENTS

The author wishes to thank Mr G. Karles for his contribution to the experimental part of this study.

REFERENCES

- Figge, K. and Koch, J. *Fund. Cosmet. Toxicol.* 1973, **11**, 975
- Kampouris, E. M. 4th Eur. Conf. Plast. Rubbers, Paris, 1974, Paper 91
- Kampouris, E. M. *Eur. Polym. J.* 1975, **11**, 705
- Kampouris, E. M., Regas, F., Rokotas, S., Polychronakis, S. and Pantazoglou, M. *Polymer* 1975, **16**, 840
- Kampouris, E. M. *Polym. Eng. Sci.* 1976, **16**(1), 59
- Figge, K. and Rudolph, F. *Angew. Makromol. Chem.* 1979, **78**, 157
- Park, G. S. and Tran Van Hoang *Eur. Polym. J.* 1979, **15**(9), 817
- Figge, K. *Prog. Polym. Sci.* 1980, **6**, 187
- Peppas, N. A. and Zieminski, K. F. Tech. Pap., Reg. Tech. Conf.—Soc. Plast. Eng. (Plast. Prog. Process., May 5–8) 1980, p. 589
- Papaspyrides, C. D. *J. Appl. Polym. Sci.* in press
- Messadi, D. and Vergnaud, J. M. *J. Appl. Polym. Sci.* 1982, **27**, 3945

- Niebergall, H. and Hartmann, M. *Lebensm.-Wiss. Technol.* 1983, **17**(5), 254
- Schmolke, R., Kamenz, P. and Kramer, H. G. *Acta Polym.* 1984, **35**(1), 110
- Dutta, P. K. and Graf, K. R. *J. Appl. Polym. Sci.* 1984, **29**(6), 2247
- Frisch, H. L. *J. Polym. Sci.* 1978, **16**, 1651
- Kretschmar, H. W., Paul, H. and Wuerthle, P. (Kretschmar, Bruno, K.-G.) Ger. (East) Patent 90428 (5 June 1972); *Chem. Abstr.* 77-153406b
- Lyon, P. J. and Clark, C. J. (Marley Tile A.-G.) S. Afr. Patent 71 06 168 (14 Mar. 1973); *Chem. Abstr.* 80-4503r
- Williams, G. E. (Armstrong Cork Co.) US Patent 4045 600 (30 Aug. 1977); *Chem. Abstr.* 87-153579s
- Vesperman, W. C. *J. Vinyl Technol.* 1979, **1**(1), 1
- Ljunggren, L. *Artif. Organs* 1984, **8**(1), 99
- Hirooka, M., Fujii, Y., Maruyama, T. and Hata, K. (Sumitomo Chemical Co. Ltd) Jpn. Kokai 75 129 701 (14 Oct. 1975); *Chem. Abstr.* 84-75281k
- Hirooka, M., Fujii, Y., Mashita, K. and Kimura, F. (Sumitomo Chemical Co. Ltd) Jpn. Kokai 75 148 503 (28 Nov. 1975); *Chem. Abstr.* 84-181298f
- Saken Kako Co. Ltd., Jpn. Kokai Tokkyo Koho JP 81 129 233 (9 Oct. 1981); *Chem. Abstr.* 96-36298z
- Congdon, W. I., Mottine, J. J. and Vesperman, W. C. (Western Electric Co. Inc.; Bell Telephone Laboratories Inc.) US Patent 4 166 881 (4 Sept. 1979); *Chem. Abstr.* 91-176418k
- Horn, P., Leppmeier, F., Eckert, G. and Fischer, K. (BASF A.-G.) Ger. Offen. 2 630 114 (19 Jan. 1978); *Chem. Abstr.* 88-137616s
- Horn, P., Leppmeier, F., Eckert, G., Fischer, K. and Reimann, H. (BASF A.-G.) Ger. Offen. 2 800 149 (12 July 1979); *Chem. Abstr.* 91-158724c
- Izumi, H. and Sahara, M. (Japan Carbide Industries Co. Inc.) Jpn. Kokai 72 03 021 (27 Jan. 1972); *Chem. Abstr.* 77-140960c
- Ichikawa, T. and Minoo, O. (Terumo K. K.) Ger. Offen. 2 542 995 (29 Apr. 1976); *Chem. Abstr.* 85-51784w
- Ichikawa, S. and Minoo, O. (Terumo Corp.) Jpn. Kokai 78 05 337 (25 Feb. 1978); *Chem. Abstr.* 89-7102f
- Oth, M. A. and Mathieu, A. *Rev. Belge Matieres Plast.* 1968, **9**(5), 307
- Nissin Electric Co. Ltd, Jpn. Kokai Tokkyo Koho JP 58 208 372 (83 208 372) (5 Dec. 1983); *Chem. Abstr.* 100-122955u
- Bowmer, T. N., Hellman, M. Y., Taylor, G. N. and Vroom, W. I. *Org. Coat. Appl. Polym. Sci. Proc.* 1983, **48**, 496
- Tadashi, K. *Sci. Ind.* 1965, **39**, 753
- Asai, M., Tsuda, K. and Okata, A. (Agency of Industrial Sciences and Technology) Ger. Offen. 2 847 304 (3 May 1979); *Chem. Abstr.* 91-21779e
- Asai, M., Tsuda, K. and Oka, H. (Agency of Industrial Sciences and Technology) Jpn. Kokai Tokkyo Koho 79 64 573 (24 May 1979); *Chem. Abstr.* 91-158573c
- Asai, M., Suda, Y., Imada, K., Ueno, S. and Nomura, H. (Agency of Industrial Sciences and Technology; Shin-Etsu Chemical Industry Co. Ltd) Ger. Offen. 3 016 048 (6 Nov. 1980); *Chem. Abstr.* 94-31510m
- Toray Industries Inc., Jpn. Kokai Tokkyo Koho 80 121 049 (17 Sept. 1980); *Chem. Abstr.* 94-31627e
- Toray Industries Inc., Jpn. Kokai Tokkyo Koho 80 121 050 (17 Sept. 1980); *Chem. Abstr.* 94-31628f
- Imada, K., Ueno, S., Nishina, Y. and Nomura, H. (Shin-Etsu Chemical Industry Co. Ltd) Fr. Demande 2 469 426 (22 May 1981); *Chem. Abstr.* 95-170503v
- Mitsubishi Monsanto Chemical Co.; Shin-Etsu Chemical Industry Co. Ltd, Jpn. Kokai Tokkyo Koho JP 58 224 746 (83 224 746) (27 Dec. 1983); *Chem. Abstr.* 100-157910c
- Mitsubishi Monsanto Chemical Co.; Shin-Etsu Chemical Industry Co. Ltd, Jpn. Kokai Tokkyo Koho JP 58 224 800 (83 224 800) (27 Dec. 1983); *Chem. Abstr.* 100, 157673c
- Kwei, K.-P. S. *J. Polym. Sci. (A-1)* 1969, **7**, 1075
- Sobue, H., Tabata, Y. and Tajima, Y. *J. Polym. Sci.* 1958, **XXVII**(115), 596
- Rånby, B. and Rabek, J. F. in 'Photodegradation, Photo-oxidation and Photostabilization of Polymers', Wiley-Interscience, New York, 1975
- Gibb, W. H. and MacCallum, J. R. *Eur. Polym. J.* 1971, **7**, 1231
- Gibb, W. H. and MacCallum, J. R. *Eur. Polym. J.* 1972, **8**, 1223
- Park, G. S. in 'Diffusion in Polymers', (Eds. J. Crank and G. S. Park), Academic Press, London, 1968
- Alfrey, T., Gurnee, E. F. and Lloyd, W. G. *J. Polym. Sci. C* 1966, **12**, 249