Macromol. Symp. ***129,*** *99–108 (1998)*

SURFACE MODIFICATION OF POLYOLEFINS BY PHOTOGRAFTING OF ACRYLIC MONOMERS

C. Decker, K. Zahouily

Laboratoire de Photochimie Générale (URA-CNRS N°431)
Ecole Nationale Supérieure de Chimie - Université de Haute-Alsace
3, rue Alfred Werner- 68200 Mulhouse (France)

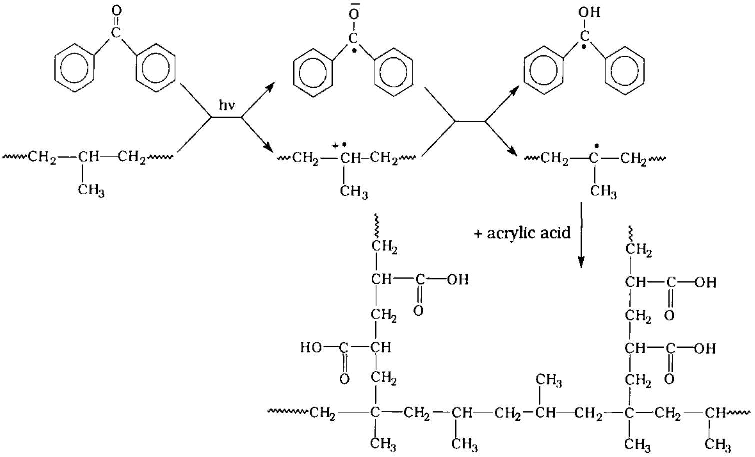
Abstract : High-speed surface modification of polypropylene (PP) and polyethylene (PE) films has been achieved by liquid phase photograft polymerisation of acrylic acid (AA) and hydroxypropyl acrylate (HPA). Benzophenone was used as photoinitiator to generate polymer radicals at the surface of the polyolefin film. The grafting reaction was carried out in aqueous solution or with the neat monomer, which was laminated between two PP films, in the presence of air. Under the intense illumination of a UV-curing line, acrylic acid was grafted within seconds to polypropylene films or fabrics, which were thus made hydrophilic. Direct evidence of surface grafting was obtained through infrared spectroscopy analysis and surface energy measurements. This continuous photografting process proved to be very efficient to improve the adhesion of UV-cured acrylate coatings on polyolefin-made materials.

INTRODUCTION

Photoinitiated graft polymerisation is one of the fastest and most efficient methods to modify durably the surface properties of organic substrates. This technology has been successfully applied to various polymers [1,2], in particular to polyolefins [3-11], to improve adhesion and surface wettability. By selecting the proper monomer, e.g. acrylic acid, acrylamide or glycidyl methacrylate, polyethylene and polypropylene-made materials have been render hydrophilic or have been functionalised with reactive groups [7,8,11]. The originality of the photochemical process lies in the fact that the radical sites are produced only at the surface of the polymer, by UV irradiation in the presence of a photoinitiator. These polymer radicals will then initiate the polymerisation of an overlaying monomer coated onto the polymer substrate.

The photoinitiator must be of the hydrogen-abstraction type, like benzophenone or thioxanthone. When excited by UV-light, these compounds are known to interact with organic compounds by electron transfer, followed by proton transfer, to give the inactive ketyl radical [12]. If the alkyl radical formed at the same time on the polymer molecule reacts with the surrounding monomer molecules, it will generate a polymer chain grafted at the surface of the substrate. The grafting reaction of acrylic acid onto polypropylene, photoinitiated by benzophenone, can be written formally as follows :

CCC 1022-1360/98/$ 10.00



In case alkyl radicals are also generated by hydrogen abstraction from the monomer (or the solvent), grafting will be accompanied by homopolymerisation.

Because the oxygen molecule is a very effective radical scavenger, photografting of vinyl monomers is usually carried out in an inert atmosphere. The reaction needs to be performed in a specially designed photoreactor, and may last up to 6 hours [5]. A fast continuous photografting process has been recently developed by Ränby et al.[7,8], well suited to the treatment of fibers, filaments or yarns, but not for large dimension items. Moreover, the thickness of the grafted layer was found to be very small, less than 10 nm, which may affect its longterm surface characteristics and wetting performance.

The objective of the present study was to perform an efficient and fast photografting of acrylic monomers on polyolefins, by a continuous solvent-free process requiring no nitrogen purge. To make the process cost-efficient, we have used a UV-curing line, similar to those found in the coating industry, rather than a tailor-made irradiation set up. With such powerful UV lamps, the timescale of the grafting reaction was expected to be reduced to a few seconds, thus allowing high-speed treatment of large dimension items. In coating applications, one can expect adhesion to be improved by the chemical bonding between the substrate and the protective UV-cured film, and by the good surface wetting as well. Another advantage of this photoinitiated process is that the grafting reaction is only occurring in the illuminated areas, thus providing a simple method to produce high resolution images of controlled hydrophilicity.

EXPERIMENTAL PART

Materials

Benzophenone (BZP) from Merck was selected as hydrogen abstraction type photoinitiator for most grafting experiments. Its UV absorption range extends from 250 to 340 nm, which means that any glass-ware filtering UV radiation of wavelength below 330 nm should be avoided, in order to generate efficiently the excited BZP molecules. The photoinitiator was dissolved in the neat monomer or in an aqueous monomer solution containing a surfactant (0.5% of Lutensol ON 70 from BASF). The following acrylic monomers were used as received without further purification : acrylic acid (AA) from Merck, hydroxypropyl acrylate(HPA) from UCB, and hexanediol diacrylate (HDDA) from UCB. A typical aqueous formulation contained 30% monomer, 69% water, 0.5% photoinitiator and 0.5% surfactant. The grafting reaction was performed on commercial transparent polypropylene (PP) or polyethylene (PE) films (~ 50 μm thickness), or on non-woven PP or PE fabrics.

Irradiation

The monomer formulation was laminated between two polymer films, at a typical thickness of 50 μm for the aqueous solution and 10 μm for the neat monomer. Samples were exposed shortly to the UV radiation of a medium pressure mercury lamp from IST (80 W cm^{-1}), which has its main emission lines between 248 and 578 nm. The light emitted was focused by means of a semi-parabolic reflector onto a 8 cm wide area, where the UV intensity was measured by radiometry to be 600 mW cm^{-2} or 1.8×10^{-6} einstein s^{-1} cm^{-2}. The sample was placed on a moving conveyor and passed under the lamp at a typical speed of 5 m/min, which corresponds to an exposure time of 1 s. Most industrial UV-curing lines are equipped with two or three UV lamps, and they can treat up to 2 m wide items by a continuous process. At the indicated belt speed, the grafting of two 300 m long PP foils could be achieved within 1 hour.

All the irradiation experiments described in this paper have been performed in the presence of air, with air-saturated solutions. Diffusion of atmospheric oxygen during the UV exposure was prevented by the laminated PP film. After irradiation, the two grafted films were separated, thoroughly washed with water to remove unreacted monomer, residual photoinitiator and homopolymer, and dried at ambient temperature.

Analysis

Infrared transmission spectroscopy was used both to monitor the photoinitiated polymerisation of the monomer through the decrease of the acrylic double bond at 810 cm^{-1}, and to characterise the grafted acrylic monomer through its carbonyl absorbance around 1700 cm^{-1}. The superficial layer of the grafted sample was also analysed by IR multiple internal reflectance (MIR), by means of a ZnSe 45° crystal.

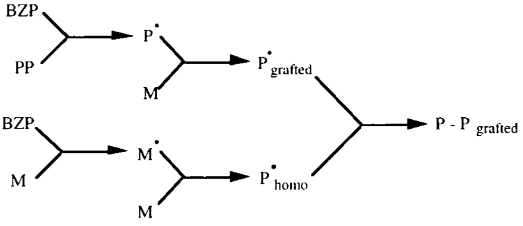
Modifications of the polymer surface energy upon grafting were quantified by measuring the static contact angle of water, formamide or tricresylphosphate (Digidrop from GBX Instruments). The image of the droplet deposited on the sample which appears on the screen allows an accurate evaluation of the contact angle. The dispersive (γ_{LD}) and polar (γ_{LP}) components of the surface energy were determined from the linear plot of $\gamma_L (1 + \cos\theta)/2\ \gamma_{LD}^{0.5}$ versus $(\gamma_{LD}/\gamma_{LP})^{0.5}$, by using the Owens-Wendt equation [13].

PHOTOGRAFTING IN AQUEOUS SOLUTION

Acrylic acid

In a typical experiment, an aqueous solution of acrylic acid (30 wt%), benzophenone (0.5 wt%) and Lutensol ON 70 (0.5 wt %) was laminated between two transparent polypropylene films, and exposed to UV radiation for a few seconds. After 3 passes under the mercury lamp, acrylic acid was shown to have polymerised from the decrease of the double bond IR absorbance at 810 and at 1630 cm^{-1}. The fact that polymerisation proceeds less extensively when the same solution was UV exposed between two BaF_2 crystal is already an indication that the PP substrate has contributed to the initiation step through its abstractable hydrogen atoms.

Direct evidence demonstrating that grafting has indeed occurred has been obtained by two sets of experiments. In the first one, the two laminated PP films were separated after UV irradiation and soaked in water to wash away any soluble homopolymer. After drying the film at 70°C, the presence of grafted poly(acrylic acid) was clearly shown by IR spectroscopy analysis, with a characteristic peak centered at 1670 cm^{-1} due to the carboxylic group. From the height of this peak, the thickness of the grafted superficial layer was evaluated to be on the order of 2000 nm. The thickness of the grafted layer can be finely controlled by acting on the exposure time and on the acrylic acid concentration. Such a high value suggests that the insoluble material consists not only of poly(acrylic acid) grafted on the PP surface, but also of some homopolymer chemically bonded to PP by radical recombination, and which cannot be washed away during aqueous development.



Another argument in favour of photografting is provided by surface energy measurements. The contact angle of water was found to drop from an initial value of 90° for the untreated PP to a value as low as 30° for the UV-irradiated film. Figure 1 shows how the contact angle of water on PP or PE films decreases with the UV exposure time. Drastic surface modification by grafting was already achieved after 1 s in both samples. Photografting of acrylic acid in aqueous medium appears as an easy and fast way to make polyolefins items hydrophilic and increase markedly their wettability. It should be noticed that the grafted carboxylic groups can be used to induce some further surface modification, by promoting chemical reactions on the functionalised polyolefins, for instance with the epoxy groups of a telechelic oligomer.

Similar results have been obtained by impregnating a non-woven PP fabrics with the same aqueous solution of acrylic acid, and exposing it to UV radiation between two PP films. From the weight increase of the fabrics, after water washing and drying at 90°C, the grafting yield was

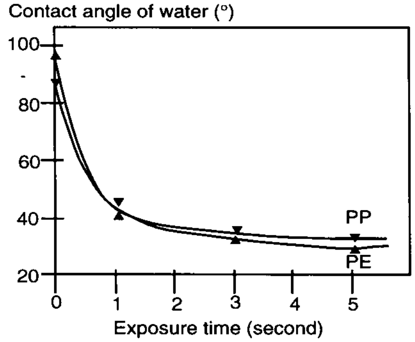


Fig.1 : Influence of the exposure time on the wettability of polypropylene or polyethylene film grafted with acrylic acid

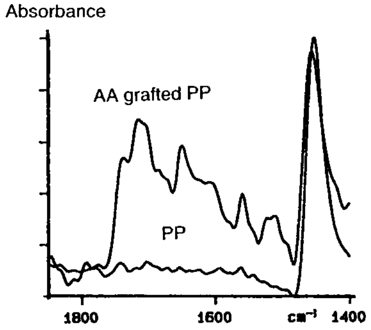


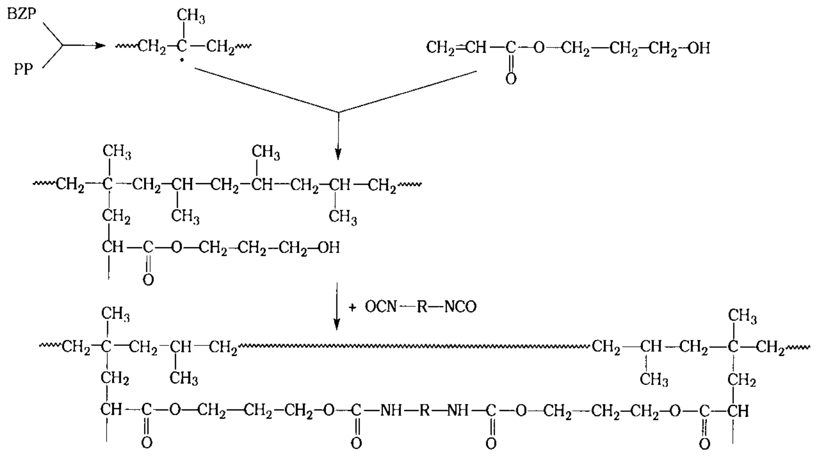
Fig.2 : Infrared spectra of polypropylene before and after photografting with acrylic acid

measured to be on the order of 15% after a 5 s exposure on each side of the 5 mm thick sample. As expected, its value was found to increase as the diameter of the fibre was decreased, reaching 40% for 4 µm thick fibres. In a polyethylene fabrics, the grafting reaction proceeds nearly as efficiently as in PP, which indicates that both secondary and tertiary hydrogens of PP are abstractable and produce initiating sites. The presence of grafted acidic groups was demonstrated by both IR spectroscopy analysis (Fig.2) and by capillarity measurements. The rate of capillary ascension of water was found to increase from an initial value of 0 for the untreated fabrics (no capillarity) to a value of 7 m/min for the photografted PP sample. It should be mentioned that, by this process, the two PP films serving to laminate the sample are being grafted at the same time as the fabrics, specially the one exposed directly to UV radiation.

A hydrophilic image was obtained by exposing the laminated fabrics through a mask. It was made apparent by dipping the sample into an aqueous solution of methylene blue. The dye was only absorbed in the light exposed areas made hydrophilic by photografting. This process could thus be visualised easily and quantified through the coloured image.

Hydroxypropyl acrylate

Another series of grafting experiments has been performed on PP films and fabrics by using hydroxypropyl acrylate (HPA) as monomer, at the same concentration (30 wt%). The polymerisation developed nearly as efficiently as with acrylic acid, the grafting yield reaching values of up to 30%. Here, it is the presence of the polar hydroxy groups on the grafted chains which renders the grafted surface hydrophilic (contact angle of water : 40°). The pendant OH groups of the macroglycol chains may serve to promote some further reaction by grafting of a second monomer. For instance, a polyurethane coating can be formed on top of the polypropylene foil by simple reaction of the polyol with a di-isocyanate, according to the following scheme :



PHOTOGRAFTING OF LIQUID ACRYLIC MONOMERS

Hydrophilic monomers

A solvent-free method of photografting was also used to modify the surface characteristics of polyolefins. The liquid monomer (AA or HPA) containing the photoinitiator (2 wt% of benzophenone) was laminated between two PP films. Although wetting of PP by HPA is quite poor, a uniform film was obtained when the second PP film was placed on top of the liquid monomer. After UV radiation (1 pass at 5 m/min), the two films were separated and washed thoroughly to eliminate the water soluble homopolymer. Figure 3 shows the IR spectra in the carbonyl region of polypropylene and polyacrylate grafted polypropylene. Surface analysis by MIR infrared spectroscopy has confirmed the presence of a grafted polyacrylate layer of about 500 nm thickness.

The photografting of polypropylene with polar monomers leads to a sharp increase of the surface free energy (γ), from an initial value of 23.7 mJ cm^{-2} to 60.7 mJ cm^{-2} for the sample grafted with acrylic acid. Figure 4 shows a typical Owens-Wendt plot for virgin and UV grafted PP films. From these curves the dispersive component (γ_D) and polar component (γ_P) of the surface free energy were calculated. With acrylic acid, γ_D was found to remain essentially constant, passing from 18.8 to 20.7 mJ cm^{-2} after surface treatment, whereas γ_P increased from 4.9 to 40 mJ cm^{-2} at the same time. By using HPA as monomer, the results obtained were essentially the same as with acrylic acid, specially regarding the polar component of the surface energy : γ_P = 38.8 mJ m^{-2}. A very similar trend was observed with acrylic acid grafted polyethylene, where γ_P reached an even higher value : 44.6 mJ m^{-2}. As a result of the increased hydrophilicity, the treated polyolefin foil can be printed with aqueous-based inks. Table 1 summarises the surface energy data obtained by photografting of PP and PE samples.

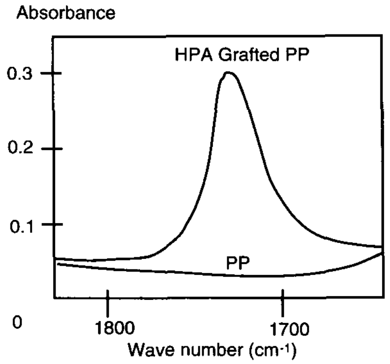


Fig. 3 : Infrared spectra of polypropylene, before and after photografting with hydroxypropyl acrylate

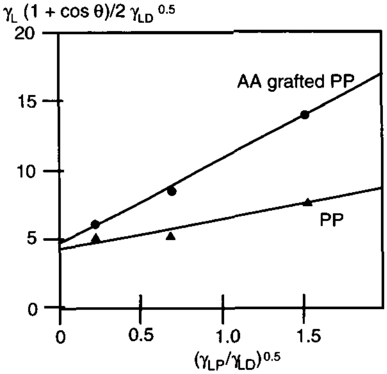


Fig.4 : Owens-Wendt plot of the surface energy for polypropylene and acrylic acid grafted polypropylene

	POLYPROPYLENE			POLYETHYLENE	
Grafting	no	AA	HPA	no	AA
γ_D (mJ m-2)	18.8	20.7	18.9	23.4	20.0
γ_P (mJ m-2)	4.9	40	38.8	3.0	44.6
γ_{total} (mJ m-2)	23.7	60.7	57.7	26.4	64.6

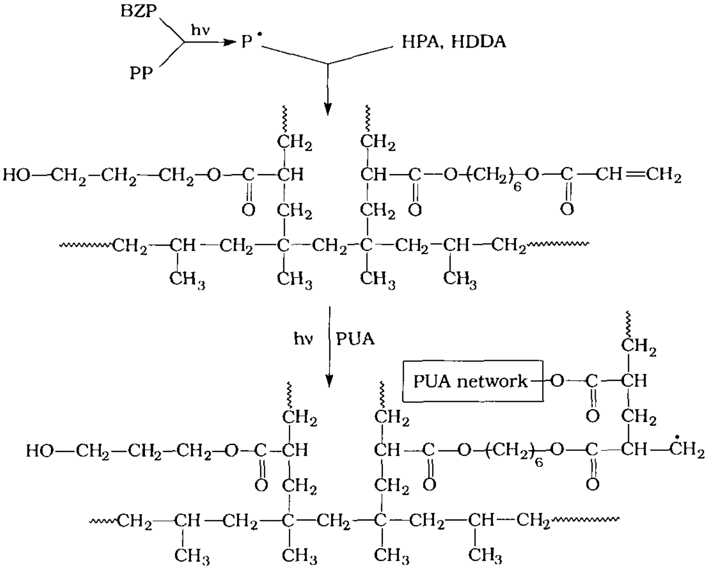
UV-curable acrylate resins

Organic coatings are commonly used to improve the surface characteristics of different types of materials (metals, plastics, glasses, paper, wood, etc...), and prolonge their service life. While most of the systems utilised today are solvent-based, there is a growing interest for solvent-free formulations, because of environmental concern. In this respect, UV-curable coatings appear as a promising alternative, as this technology offers the advantages of high-speed curing, low VOC emission, low energy consumption and ambient temperature operations. However, film shrinkage due to the rapid polymerisation, together with poor substrate wetting, may cause adhesion failure, specially on plastics with low surface energy.

Photografting of hydrophilic monomers may constitute a possible solution to improve the adhesion, not only because it creates chemical bonds at the coating/substrate interface, but also because it provides a better wetting by the liquid UV-curable formulation. This approach has been successfully used to protect PVC plates by UV-cured acrylate coatings [2,14]. Good wetting is achieved when the surface energy of the coating formulation is lower than that of the substrate [15].

UV-curable acrylate resins have surface energy values which range typically between 30 and 40 mJ m^{-2}, while the γ value of polyolefins is substantially lower (23-30 mJm^{-2}). This leads to poor wetting and poor adhesion of the UV-cured coating which tends to delaminate. Photografting of polar monomers might be a simple solution to this problem, as this reaction was previously shown to increase markedly the surface energy of polypropylene : γ = 57.7 mJ m^{-2} after grafting of HPA.

The basic idea behind this work was to achieve an effective and longlasting protection of polyolefin made materials by performing a 2-step photografting process of acrylic coatings : (i) a photografting of a mixture of hydroxypropylacrylate (HPA) and hexanedioldiacrylate (HDDA) and (ii) a photoinduced copolymerisation of a UV-curable polyurethane-acrylate resin (PUA) with the remaining pendant acrylate double bonds of HDDA. The reaction scheme can be formally written as follows :



The addition of HDDA to the HPA-BZP formulation was found to have no detrimental effect on the grafting process. The 1/1 monomer mixture, laminated between two PP films, was shortly exposed to UV radiation (1 pass at 10 m min^{-1}) in order to keep, after solvent development, a sufficient amount of unreacted acrylate double bonds on the grafted chains. From the IR spectra recorded, it was concluded that 40% of the total acrylate double bonds had polymerised after the short irradiation. Of the remaining 60%, two thirds were eliminated as homopolymer by soaking the film in acetone. Knowing the initial acrylate concentration of the formulation (8.2 mol kg^{-1}), the amount of pendant acrylate double bonds located on the grafted chains was calculated to be 1.6 mol kg^{-1}.

In a second step, the sample was coated with the following UV-curable formulation : polyurethane-acrylate (73%), HDDA (25%), Irgacure 1700 (2%). The 30 µm thick film was cured in the presence of air by a single pass under two UV lamps, at a speed of 10 m min^{-1}. The tack-free coating showed excellent adhesion on the pretreated polypropylene foil, because of copolymerisation of the acrylate double bonds of the resin with those located on the polyacrylate grafts. In practical applications, the top coat will be applied on the still tacky film obtained after peeling off the laminated sample. The two-step coating process can therefore be carried out continuously, on a conventional UV-curing line.

By introducing light stabilisers in the coating formulation to screen the harmful solar radiation, one can substantially improve the weathering resistance of polypropylene, as was previously done for poly(vinyl chloride)[2,14]. Grafting will ensure a longlasting adhesion, and therefore prevent premature delamination, which is often observed in coated organic materials upon prolonged outdoor exposure.

CONCLUSION

Polypropylene and polyethylene foils have been superficially modified by photoinitiated grafting of acrylic acid and hydroxypropyl acrylate. With these polar monomers, the hydrophilicity and wettability of PP and PE has been drastically increased within seconds, upon UV exposure in the presence of a hydrogen abstraction-type photoinitiator. The grafting reaction was performed by a continuous process, in the presence of air, by lamination of the liquid monomer, or an aqueous solution of it, between two polypropylene films.

Grafting has been characterised by IR spectroscopy analysis and by surface energy measurements, after solvent development of the irradiated sample. By this simple process, polyolefin foils can be made suitable for printing. As grafting occurs only in the illuminated areas, one can generate high resolution images of controlled hydrophilicity by a static exposure of the sample through a mask. Another benefit of the grafting reaction is that it improves the coating-substrate adhesion, because of the chemical bonds formed at the interface. UV-curable formulations have thus been coated onto pre-grafted polyolefin foils, to get strongly adhesive protective coatings.

One of the main advantages of the photografting process reported in this work is that it is based on a well-established UV technology, and that it requires no modifications of the industrial UV-curing lines currently used. It offers the distinct features of photochemical initiation, i.e., ultrafast reaction, low energy consumption, solvent-free formulation, low VOC emission, ambient temperature operations, and on-line processing of large dimension items. For all these reasons this process should be of particular interest in the coating and printing industry, where it could open the field to new high-tech applications of polyolefin-made materials.

REFERENCES

1. G. Oster, G.K. Oster, H.J. Moroson, *J.Polym.Sci.* **34**, 671 (1959).
2. C. Decker, *J. Appl.Polym.Sci*., **28**, 97 (1983).
3. S. Tazuka, H. Kimura, *Makromol.Chem.* **179**, 2603 (1978).
4. K. Yamada, H. Tsutaya, S. Takekawa, M. Hirata, *J.Appl.Polym.Sci.* **46**, 1065 (1992)
5. H. Kubota, *J.Appl.Polym.Sci.* **48**, 1717 (1993)
6. K. Almer, J. Hilborn, P.H. Larson, A. Hult, B. Ränby, *J.Polym.Sci.*, Polym.Chem.Ed. **28**, 173 (1990).
7. Z.P. Yao, B. Ränby, *J.Polym.Sci.*, **40**, 1647 (1990).
8. Z.G. Feng, B. Ränby, *Angew.Makromol.Chem.* **195**, 17 (1992).
9. R.W. Singleton, J.A. Cook, K. Gargan WO Patent 93/01622 (1993).
10. D. Ruckert, G. Geuskens, *Eur. Polym. J.*, **31**, 431 (1995) and **32**, 201 (1996).
11. G. Bai, X. Hu, Q. Yan, *Polym.Bull.* **36**, 503 (1996).
12. N.J. Turro, *Modern Molecular Photochemistry*, Benjamin Cummings Publ.Co., Menlo Park, California, 1978, p.368.
13. D. Owens, R. Wendt, *J.Appl.Polym.Sci.* **31**, 1741 (1969).
14. C. Decker, Fr.Patent 8603002 (1986).
15. F. Mc Gill, *Polym.Paint.Col.J.* **186**, 10, (1996).