Fluorinated Epoxides as Surface Modifying Agents of UV-Curable Systems

M. Sangermano,[1] R. Bongiovanni,[1] G. Malucelli,[1] A. Priola,[1] A. Pollicino,[2] A. Recca[2]

[1]*Dipartimento di Scienza dei Materiali e Ingegneria Chimica, Politecnico di Torino, C.so Duca degli Abruzzi 24, 10129 Torino, Italy*
[2]*Dipartimento di Metodologie Fisiche e Chimiche per l'Ingegneria, Università di Catania, V.le A. Doria, 6, 92125, Catania, Italy*

ABSTRACT: Two commercially available epoxy-fluorinated monomers, 3-(perfluorooctyl)-1,2-propenoxide and 3-(1H, 1H, 9H-hexadecafluorononyloxyl)-1,2 propenoxide, were used as modifying additives for UV curable systems. These two fluorinated monomers were mixed, in small amounts (less than 1% w/w) with a hydrogenated epoxy monomer 1,4-cyclohexanedimethanol-diglycidyl ether. The mixtures were coated on glass substrate and UV-cured, giving rise to transparent films. Notwithstanding their very low concentrations, the fluorinated monomers caused a change in the surface properties of the films, without changing their curing conditions and their bulk properties. The air side of the coatings became highly hydrophobic, while the substrate side was unmodified. As shown by XPS measurements, the fluorinated monomers were able to concentrate selectively on the air side of the films, forming a fluorinated layer. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 1524–1529, 2003

Key words: fluoropolymers; cationic photopolymerization; surfaces

INTRODUCTION

The use of fluorinated monomers and oligomers for coatings is attractive due to the unique characteristics given by the presence of fluorine, such as hydrophobicity, chemical stability and weathering resistance, release properties, low friction coefficient, water impermeability and low refractive index.[1]

It seemed interesting to employ fluorinated structures in UV-curable systems; by introducing fluorinated monomers in the UV-curable systems, it would be possible to combine the properties of these molecules and the advantages of the UV curing technology, giving rise to cured products with outstanding properties. In fact, the photopolymerization process is of great interest in many industrial applications. The formulations are solvent free, the production rates are high and the energy required is much less than in thermal curing. These advantages have led to the rapid growth of the technique in different fields, mainly in the production of films, inks and coatings on a variety of substrates, including paper, metal and wood. Moreover, a variety of high-tech and electronic applications, such as the coating of optical fibers and the fabrication of printed circuit boards, have been developed.[2]
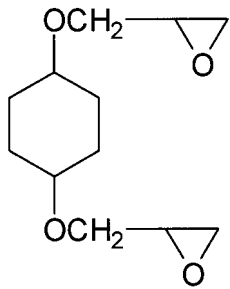
In all of these fields, the improvement in performance of the UV-cured systems is appreciable. The introduction of fluorine into the network structure guarantees unique properties, and some papers have already described the good results obtained for acrylated systems, either based on fluorinated monomers[3,4] or containing small amounts of fluorinated additives.[5–8]

In this study we extend the use of fluorinated structures to the field of cationic UV-curing, employing epoxy monomers. Photoinitiated cationic polymerization has the additional advantage of oxygen insensitivity with respect to the radical mechanism; moreover, the monomers employed, compared to the acrylate formulations of the radical photopolymerization, are less toxic and less likely to cause irritation.[9]

Taking into account the advantages of the cationic UV-curing technique over the radical mechanism, we investigated the effect of fluorinated additives on the photopolymerization of epoxy resins via a cationic pathway. Two different epoxy-fluorinated monomers were investigated in this work, 3-(perfluorooctyl)-1,2-propenoxide and 3-(1H,1H,9H-hexadecafluorononyloxyl)-1,2 propenoxide. These two fluorinated monomers were copolymerized, in different amounts, with the epoxy monomer 1,4-cyclohexanedimethanol-diglycidyl ether. The cured films were characterized with respect to their bulk and surface properties.

Correspondence to: R. Bongiovanni.

TABLE I
Structure of Monomers

Monomers	Structures	Notes
1,4-Cyclohexanedimethanolodiglycidyl ether		DGE
3-(Perfluorooctyl)-1,2-propenoxide	$CF_3(CF_2)_7CH_2$—	F1
3-(1H,1H,9H-Hexadecafluorononyloxy)−1,2 propenoxide	$H(CF_2)_8CH_2OCH_2$—	F2

EXPERIMENTAL

Materials

The fluorinated monomers 3-(perfluorooctil)-1,2-propenoxide (F1) and 3-(1H,1H,9H-hexadecafluorononyloxyl)-1,2 propenoxide (F2) were purchased from Fluorochem (England) and were used as received, checking their structures and purity by ^1H-NMR. The epoxy hydrogenated resin is 1,4-cyclohexanedimethanoldiglycidyl ether (DGE), available from Aldrich. The structures of the products are reported in Table I. Triphenylsulfonium hexafluoroantimonate ($Ph_3S^+SbF_6^-$), generously supplied from Union Carbide, was used as the cationic photoinitiator. It is available in solution with propylene carbonate (50% w/w), and it was added to the curable mixtures at a concentration equal to 2% w/w.

Film preparation

The films were obtained by coating the photopolymerizable mixtures on glass. First, solutions of the fluorinated monomers of accurate concentration were prepared. Accurate volumes of them were added to DGE, along with the photoinitiator (2% w/w). This procedure permitted control of the final concentration of the fluorinated comonomer and assured a better homogeneity of the mixtures after a careful stirring. The mixtures were spread on a glass slide with a calibrated wire-wound applicator to obtain a thickness of about 100 μm. The solvent was left evaporated in air.

The curing reaction was performed by UV irradiation with a medium pressure Hg lamp (Italquartz, Milano, Italy), provided with a water jacket. The light intensity at the film surface was 20 mW/cm^2. The irradiation was stopped when a constant epoxy conversion was found, as determined by FTIR measurements. The samples, after irradiation, were placed in a close system saturated with 5% v/v water/ammonia solution vapors for 15 min, in order to neutralize the acidic species.

The films were peeled away from the substrate; the surface in contact with the substrate was labeled as the glass side, the other as the air side.

Film characterization

The epoxy group conversion during the photopolymerization was determined by FTIR spectrometry. The process involved coating the photocurable mixture on a KBr disk and measuring the decrease of the epoxy absorption band at 848 cm^{-1}, after different periods of irradiation. The instrument used was a Genesis Series ATI Mattson (USA) Spectrometer.

The gel content of the films was determined by measuring the weight loss after 20 h of extraction at room temperature with two different solvents, chloroform and trichlorotrifluoroethane.

DSC measurements were performed with a Mettler DSC30 (Switzerland) instrument, equipped with a low temperature probe.

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MKIII (UK) instrument, at the frequency of 1 Hz in the tensile configuration.

Contact angle measurements were performed with a Kruss DSA10 instrument, equipped with a video camera; analyses were made at room temperature by means of the sessile drop technique. Three to five measurements were performed on every sample and the value averaged. The measuring liquid was doubly distilled water (γ = 72.1 mN/m).

XPS measurements were carried out on the films containing 0.2% and 1.0% w/w fluorinated additives by a VG Instrument electron spectrometer using a Mg $K_{\alpha,1,2}$ X-ray source (1253.6 eV). The X-ray source under standard conditions had been working at 100 W, 10 KV and 10 mA. The base pressure of the instrument was 5×10^{-10} Torr, and the operating pressure was 2×10^{-8} Torr. A pass energy of 100 eV and 50 eV was used for widescans and narrowscans, respectively. Depth profile information was obtained by running measurements on electrons taking off from the sample surface with angles of 90°, 45° and 25°. According to the equation $d = 3\gamma \sin \theta$, sample depths (d) are lower when the take off angle (t.o.a.) is smaller. All data analyses (linear background subtraction and peak integration) were accomplished using VGX900x (version 6) software. Binding energies were referenced to the C—H level at 285.0 eV.

RESULTS AND DISCUSSION

UV-curing

In previous works, we studied coatings that contained low amounts of acrylic monomers with perfluoroalkyl branches[6,7] or perfluoroalkylether chains[8]; we investigated the influence of the monomer structure and its concentration on film formation and on its final properties. The curing process and the bulk properties were not influenced by the presence of the fluorinated comonomers. The surface properties, on the other hand, were modified, and found to be dependent on the concentration of the monomer and on the length of the fluorinated chain, as one could expect.[6] Because the previous parameter was fixed, the surface characteristic depended on the fine chemical structure of the additives.[7]

On the basis of the results described above, in agreement with other works describing the modification of thermoplastic systems,[10–12] in order to modify epoxy coatings by copolymerizing the resins with fluori-
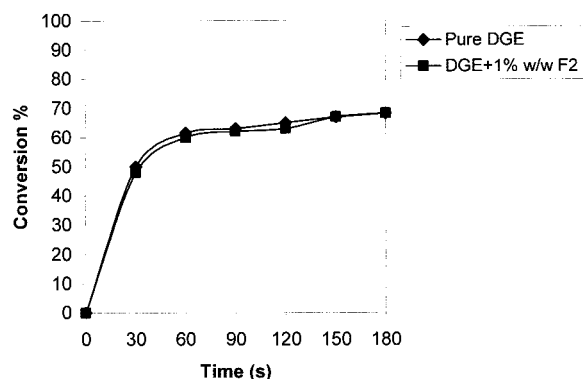

Figure 1 FTIR kinetic curves of pure DGE monomer and DGE monomer in the presence of 2 wt % F2 additive.
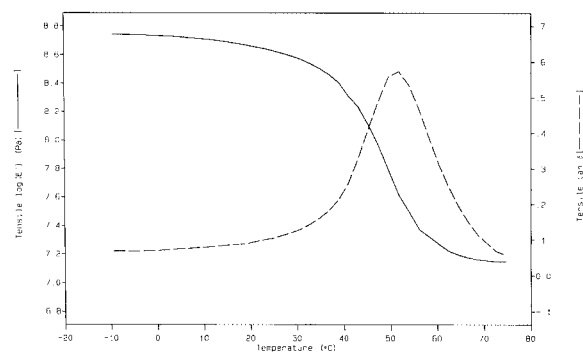

Figure 2 DMTA thermogram of UV-cured film of pure DGE.

nated monomers, we selected, among the few epoxides commercially available, those containing fluorinated chains of at least 8 carbons (monomers F1 and F2). The solubility of these monomers in the reference resin DGE was assessed by visual inspection, and the highest concentration assuring homogeneous and transparent formulations was about 1% w/w. The mixtures were coated on glass slides and, upon UV irradiation, always gave rise to transparent film, about 100 μm thick. The curing reaction in the presence of fluorinated additives showed no change from established data; the kinetics were the same as reported in Figure 1. The plots show that in the first two minutes the conversion reached 60%; further irradiating the samples, the final constant conversion equalled 70%, which corresponds to the value obtained for the pure DGE.

The cured films showed a very high gel fraction (always higher than 95%), after treatment with $CHCl_3$.

In order to check the linking of the fluorinated monomers to the epoxy network, we subjected the UV-cured film containing F2 to an extraction with trichlorotrifluoroethane, which is a good solvent for the fluoromonomer. After the extraction, the gel percentage was 97%. ^{1}H-NMR analysis was performed on the extracted solution. The fluoromonomer F2 presents a difluoromethyl group at the end of the perfluoro-carbon chain, which shows a specific signal at 6.02 ppm (HCF_2—CF_2-); a splitting triplet of triplets also characterizes the signal. On the ^{1}H-NMR spectrum of the extracted solution, it was absent; therefore the possibility of free monomer in the network can be excluded.

Bulk properties of the UV-cured films

The properties of the copolymeric networks were investigated by means of DSC and DMTA analysis. Figures 2 and 3 present the DMTA thermograms related to the pure DGE film and to a mixture of DGE in the presence of the monomer F1 at 1% w/w.
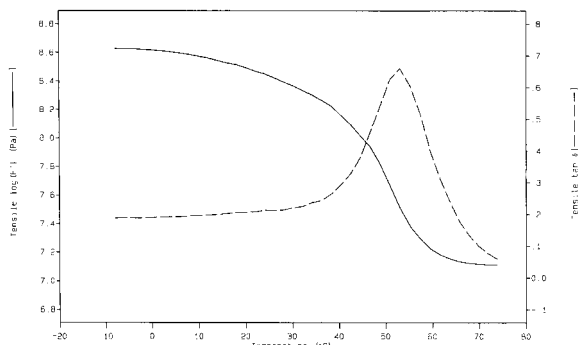
Figure 3 DMTA thermogram of UV-cured film of DGE containing 1% w/w F1.

Figure 5 Contact angle of UV-cured films plotted against concentration of F2 comonomer.

In the glass transition temperature (T_g) region, a strong decrease of E' is evident for both films, while tan δ shows a trend with a maximum. The T_g of the cured films is assumed to be at the maximum of tan δ curve, and it almost coincides for the thermograms of the two UV-cured films investigated. The T_g values were found to be independent of the presence of the fluorinated monomers; they were always equal to that of the pure hydrogenated resin (55°C).

The presence of the fluorinated additives, then, does not induce any considerable change in the network structure. The concentration of the fluorinated monomer is so low that the copolymeric films maintain the same bulk properties.

Surface properties of the UV-cured films

Contact angle measurements were performed, with bidistilled water, on all of the UV cured films. The contact angle of the pure DGE was around 70° on the glass side and 72° on the air side. When a fluorinated monomer was added to the curable product and the mixture was coated on a glass substrate, the wettability changed, as evidenced in Figures 4 and 5. The data clearly show that both additives are effective only at
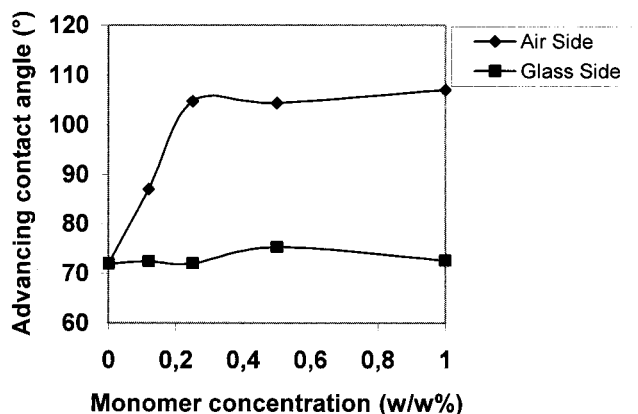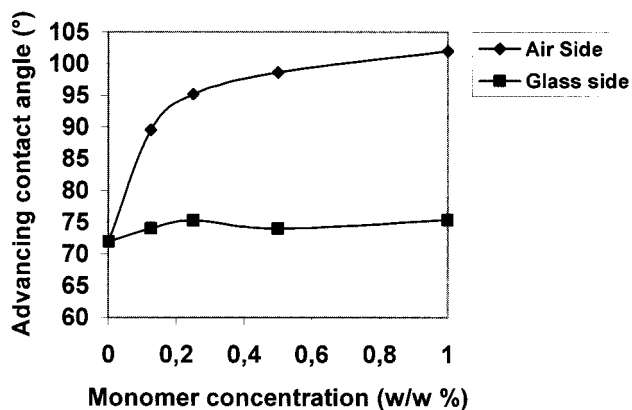

Figure 4 Contact angle of UV-cured films plotted against concentration of F1 comonomer.

the air side of the film, making it hydrophobic, while the side in contact with the substrate keeps the same properties as the pure DGE monomer. The contact angle values on the air side depend on the additive concentration with an asymptotic behavior.

Although the bulk properties of the UV-cured films are practically unchanged by the presence of the fluorinated additive, the surface properties are strongly modified. The hydrophobicity reached by addition of the fluoromonomers is very high and similar to that exhibited by fully fluorinated polymers. The surface modification, as extensively discussed in the literature on polymer blends,[13-14] copolymers,[15] and polymeric solutions[16] is a consequence of the surface segregation of low surface components, in this case the fluorinated epoxides.

Further comparing the two curves, one can see that, using monomer F1, the film becomes hydrophobic ($\theta > 90°$) by the addition of a smaller amount of fluorinated additive; moreover, the maximum value of θ is higher in the presence of F1. A similar effect was shown in a previous work[17] concerning perfluoropolyether systems with different fluorinated end groups. This difference could be due to the structure of the epoxy monomers. In particular, the better surface activity of F1 could be related to the presence of perfluoromethyl end groups, whose surface free energy is the lowest among the fluorocarbon groups, as discussed in the original work of Zisman.[18]

Besides the contact angle, further information on the film surfaces are obtained by the contact angle hysteresis, the difference between the advancing and the receeding angle.[19] For the pure DGE film, its value was found to be 16° for the air side and 14° for the glass side. As far as the glass side is concerned, in the presence of the fluorinated additives, almost no change in the hysteresis was observed. In contrast, on the air side, there was an increase of hysteresis with an asymptotic trend, clearly dependent on the monomer concentration, as observed in Figure 6. This phenom-
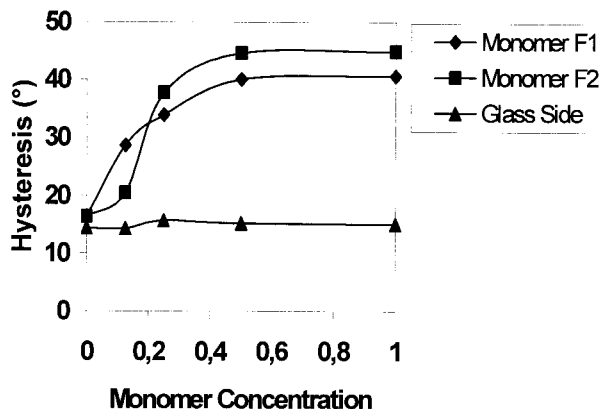
Figure 6 Film hysteresis plotted against concentration of F1 and F2 comonomers.

enon is connected to the increase in chemical heterogeneity of the surface.

X-rays photoelectron spectroscopy analyses

The surface modification of the films evidenced by the measurement of their wettability is confirmed by analyzing the surface composition of the systems. As far as the fluorine and the oxygen concentrations are concerned, the results of the air side of some of the films are reported in Table II, together with the value cal-

TABLE II
XPS Results at Different Take-Off Angles (t.o.a)

Sample take-off (°) angle (t.o.a)	F1/C1 (Atomic ratio)	O1/C1 (Atomic ratio)
DGE + 0.2% w/w F1		
25	1.072	0.174
45	0.992	0.200
90	0.859	0.219
DGE + 1.0% w/w F1		
25	1.460	0.126
45	1.421	0.136
90	1.147	0.174
DGE + 0.2% w/w F2		
25	1.010	0.203
45	0.782	0.250
90	0.605	0.282
DGE + 1.0% w/w F2		
25	1.292	0.139
45	1.190	0.192
90	0.980	0.226

Calculated value	F1s/C1s (Atomic ratio)	O1s/C1s (Atomic ratio)
DGE	–	0.33
F1	1.545	0.091
F2	1.583	0.18
DGE + 0.2% w/w F1	0.003	0.329
DGE + 1.0% w/w F1	0.015	0.327
DGE + 0.2% w/w F2	0.003	0.329
DGE + 1.0% w/w F2	0.015	0.328

culated on the basis of the mixture composition. The fluorine content determined experimentally is one order of magnitude higher than the calculated ones. When the amount of monomer is 1% w/w, the F/C ratio of the external layers of the films (t.o.a. = 25°) approaches the value of the pure additive.

Due to the fact that the concentration of fluorine in the external layers much higher than that in the bulk, one can explain the change of hydrophobicity revealed by the contact angle measurements presented earlier. The surface is mainly composed of the fluorinated comonomer, whose concentration reaches 95% w/w in the case of the film containing 1% w/w F1.

It was shown by the contact angle results that F2 is less effective in changing surface properties; in fact, we see that its surface concentration is always lower than the corresponding films containing F1. When the bulk concentration is 1% w/w, the outer layer of film contains about 63% of the fluorinated additives.

At different take-off angles (t.o.a.), the F1/C1 ratio is different and shows the existence of a concentration gradient, from the inner (higher t.o.a.) to the external surface. This is well evidenced in Figures 7 and 8, where the F/C ratio is reported against the different take-off angles for the two fluorinated comonomers employed. The F/C values on the glass side of the films were zero.
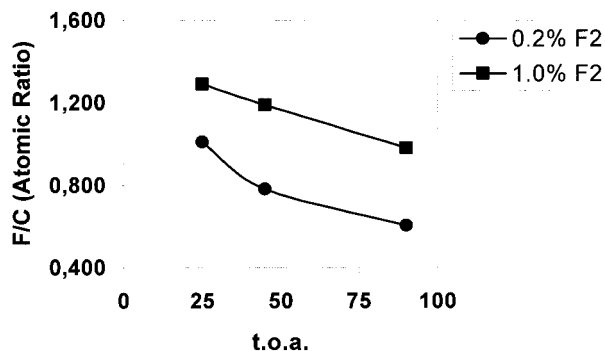

Figure 7 F/C atomic ratio plotted against take-off angle (t.o.a) of UV-cured DGE–F1 films.

Figure 8 F/C Atomic ratio plotted against take-off angle (t.o.a) of UV-cured DGE–F2 films.

While the fluorine content is higher in the surface than in the bulk, the oxygen content decreases toward the external layers of the films. At the highest t.o.a., the O/C ratio approaches the calculated value of the hydrogenated resin. This confirms the preferential distribution of the additives towards the air interface.

CONCLUSIONS

The copolymerization of epoxydized fluorinated monomers with a hydrogenated epoxy resin was performed by the UV curing technique. The bulk and surface properties of the UV cured films were investigated.

The UV cured films were transparent and, in the presence of fluorinated additives, maintained the same bulk properties. No change in the T_g value or in the kinetics of photopolymerization was observed. This is because of the low amount of the additive (its maximum solubility was always 1% w/w) in the mixture.

On the other hand, the surface properties of the UV cured films, in the presence of the fluorinated additives, were drastically changed. A selective migration to the air surface of the UV cured film was observed. As a consequence, the films became hydrophobic on the air side.

Comparing the two additives, a difference in the hydrophobic character of the films obtained by their introduction in the network was observed. The surfaces were found to have different chemical compositions by XPS analyses. In conclusion, it was shown that the chemical structure of the additives, not only their fluorine content, is important to the surface modification of the films.

References

1. Thomas, R. In Fluoropolymers 2: Properties; Hougham, G., Johns, K., Cassidy, P. E., Davidson, T., Eds.; Plenum Press: New York, 1999; Chapter 4.
2. Fouassier, J. P.; Rabek, J. C. Radiation Curing in Polymer Science and Technology; Gouassier, Ed.; Elsevier: London, 1993.
3. Bongiovanni, R.; Malucelli, G.; Pollicino, A.; Priola, A. J Appl Polym Sci 1997, 63, 979.
4. Priola, A.; Bongiovanni, R.; Malucelli, G.; Pollicino, A.; Tonelli, C.; Simeone, G. Macromol Chem Phys 1997, 198, 1893.
5. Torstensson, M.; Ranby, B.; Hult, A. Macromolecules 1990, 23, 126.
6. Ameduri, B.; Bongiovanni, R.; Malucelli, G.; Pollicino, A.; Priola, A. J Polym Sci Part A: Polym Chem 1999, 37, 77.
7. Ameduri, B.; Bongiovanni, R.; Lombardi, V.; Pollicino, A.; Priola, A.; Recca, A. J Polym Sci Part A: Polym Chem 2001, 39, 4227.
8. Bongiovanni, R.; Malucelli, G.; Priola, A.; Tonelli, C.; Simeone, G.; Pollicino, A. Macromol Chem Phys 1998, 199, 1099.
9. Crivello, J. V.; Lai, Y.-L.; Malik, R. Cationic Polymerisation, Fundamentals and Applications; Faust, R., Shaffer, T. D., Eds.; ACS Symposium Series 665; American Chemical Society: Washington, DC, 1997.
10. Pospiech, D.; Jehnichen, D.; Haubler, L.; Voigt, D.; Grundke, K.; Ober, C. K.; Korner, H.; Wang, J. Polymer Prepr; ACS Div of Polym Chem, 1998, 39(2), 882.
11. Morita, M.; Ogisu, H.; Kubo, M. J Appl Polym Sci 1999, 73, 1741.
12. Thomas, R.R. et al. Macromolecules 1997, 30, 2883.
13. Pan, D. H.; Prest, W. M. J Appl Phys 1985, 58, 2861.
14. Bhatia, O. S.; Pan, D. H.; Koberstein, J. T. Macromolecules 1988, 21, 2166.
15. Schmitt, R. L.; Gardella, J. A.; Magill, J. H.; Salvati, L. Macromolecules 1985, 18, 2675.
16. Gaines, G. L. J Chem Phys 1969, 73, 3143.
17. Bongiovanni, R.; Beamson, G.; Mamo, A.; Priola, A.; Recca, A.; Tonelli, C. Polymer 2000, 41, 409.
18. Hare, E. F.; Shafrin, E. G.; Zisman, W. A. J Phys Chem 1954, 58, 236.
19. Wu, S. In Polymer Interface and Adhesion; M. Dekker: New York, 1982, Chapter 4.