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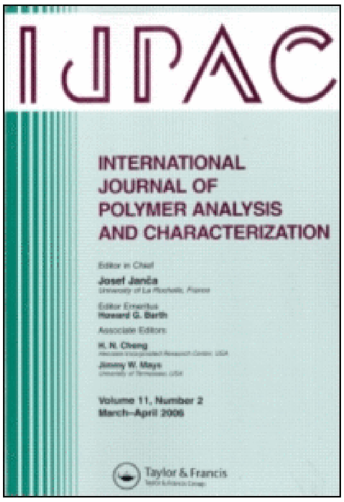

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New Segmented Polyurethanes Containing Perfluoropolyether Blocks 1. Morphological Characterization

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New Segmented Polyurethanes Containing Perfluoropolyether Blocks
1. Morphological Characterization

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The morphology of a new class of segmented polyurethanes (PU) containing perfluoropolyethers soft blocks was investigated by SEM and TEM. Effective, selective staining was obtained using ruthenium tetroxide that easily reacts with PU hard phase, leaving the fluorinated soft phase unaltered. The presence of both a micro- and a macro-phase separation was revealed. Various morphological features including shell-core structures and crystalline lamellae were detected, depending on composition and synthesis procedures. The macrophase separation was related to the immiscibility of the fluorinated macromers with the other components and to its segregation during the prepolymer formation step. The consequent formation of fluorine-rich molecules that self-segregate and the related compositional heterogeneity of the polymer chains lead to the attainment of a multiphase materials more similar to a blend than to a real statistical segmented copolymer.

Keywords: Polyurethanes, perfluoropolyethers, copolymers, morphology

INTRODUCTION

The development of a new family of perfluoropolyethers (PFPE) with reactive functional end groups, marketed under the tradename Fomblin Z® by Ausimont SpA,[1] has provided new macromers as building blocks

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for segmented copolymers with improved properties.[2] The inclusion of PFPE results in some interesting properties, such as low glass-transition temperature, high chemical stability, thermal resistance, and low surface energy because of the soft blocks of the segmented block copolymers. These macromers are used to synthesize new polyamides,[3] polyimides,[4] epoxies,[5] polyetheresters.[6–9] Moreover, polyurethanes (PU) containing PFPE, as the soft block, were recently synthesized an characterized.[10–14]

These materials have shown promising properties as thermoplastic elastomers that combine abrasion resistance and tensile strength, typical of polyurethanes, with the beneficial PFPE properties mentioned above, resulting in improvements in term of toughness in very low temperature ranges, surface characteristics, and processability. However, the total substitution of the polyethers and polyesters macromers, commonly used as soft blocks in PUs, with PFPE, presents economical drawbacks since PFPE is still rather expensive. Therefore, a new approach based on the use of partially fluorinated soft phases prepared by mixing hydrogenated and perfluorinated macromers has been devised. Some preliminary results that were presented recently,[12–13] described the possibility of obtaining significant changes in surface characteristics and in processability, even in the case of very low concentrations of PFPE.

Among the various aspects controlling PU properties, phase morphology plays a major role and its control and characterization deserve special attention. Although phase separation and morphology of segmented PUs have been studied for more than 30 years, several points still need to be clarified. The microphase separation of hard and soft domains is an established feature, but the structure of the interface and interphase, the nature of the crystalline phase, the kinetics of phase separation, and the phase transitions are still under debate. In addition, because of the peculiar chemical characteristics of fluorinated polymers and of PFPE in particular, a novel copolymer constituent, one would expect potential unusual aspects of phase separation that should be explored.

The present paper is the first of a series devoted to the investigation of morphology-properties relationships of PFPE-containing PUs and will specifically deal with the methodological and practical issues in the characterization of the morphology of this new class of polyurethanes.

EXPERIMENTAL

Synthesis

The fluorinated macrodiol used for the preparation of fluorinated polyurethanes was Fomblin ZDOLTX®; its general formula is:

$$H(OCH_2CH_2)_nOCH_2CF_2O(CF_2CF_2O)_p(CF_2O)_qCF_2CH_2O(CH_2CH_2O)_nH$$

where $n = 1,2$ and $p/q = 0.8–1.2$.

PUs, containing both hydrogenated and fluorinated macrodiols (HFPU), were prepared by a three-step procedure to optimize the fluorinated-block dispersion in the soft phase. First, the hydrogenated macrodiol, poly(tetramethylenether glycol) (PTMEG) or polycaprolactone (PCL), (molecular weight ranging from 1,000 to 2,000), was reacted in bulk, under nitrogen atmosphere, with twice the molar quantity of methylene diphenylene diisocyanate (MDI) at 90°C for 2 h to produce NCO-terminated macrodiols, PFPE ZDOLTX® then (Ausimont SpA, Milan, Italy) was added dropwise under vigorous stirring and the reaction mass was left under vacuum for 2 h. The reaction of hydrogenated and fluorinated macromers is favored by this procedure. The remaining amount of MDI, required by the selected stoichiometry, was added. Chain extension with butanediol (BDO) was conducted under stirring at 70°C for some minutes. Before the viscosity increased greatly, the mass was poured into a mold, let set for 2 min at 220°C, cooled at 130°C, let set at 130°C for 7 h, and finally cooled down to room temperature. Cast plates of about two-mm thick were obtained, stored for at least 2 weeks at room temperature and used for characterization. The materials and their composition are listed in Table I.

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Morphological Analysis

The surfaces of cryogenically fractured specimens, gold sputtered with an AgarAid model P33, were observed with a scanning electron microscope (SEM), Cambridge Stereoscan model 440 at 20 KV; X-ray microanalysis was performed with a Link Gem model Oxford.

Transmission electron microscopy (TEM) was performed on samples stained by exposure of the bulk specimen and of the thin sections to vapors

TABLE I Compositional characteristics of polyurethanes examined

*Component**	*HFPU1*	*HFPU2*	*HFPU3*	*FPU4*	*HFPU5*
MDI	3.0	2.0	3.0	2.5	2.0
ZDOLTX2000	0.2	0.2	0.3	1.0†	0.3
PTMEG2000	—	—	0.7	—	—
PTMEG1000	0.8	—	—	—	—
PCL1250	—	0.8	—	—	0.7‡
BDO	2.0	1.0	2.0	1.5	1.0
Hard Phase, wt%	43.5	29.6	32	19.2	22.7
Fluorine, wt%	11.5	12.3	12.6	47.9	14.2

*MDI: diphenylene diisocyanate; ZDOLTX: fluorinated macrodiol; PTMEG: poly(tetramethylene ether glycol); PCL: polycaprolactone; BDO: butanediol
†MW = 3,400
‡MW = 2,000

of osmium tetroxide (O_sO_4) or ruthenium tetroxide (RuO_4) aqueous solutions for different times as specified in the text.

Thin sections were ultramicrotomed at –130°C with a Reichert Ultramicrotome model OM-U2, equipped with a diamond knife, and observed at 100 KV with a Siemens Elmiskop 1101 transmission electron microscope.

RESULTS

Morphological analysis is concerned with the nature of the phase: its size, interfacial characteristics, and development. To this purpose, microscopic techniques with different resolution degrees have been applied. Optical microscopy was attempted but it proved to have insufficient resolution to clearly identify the phases which are in the micron and submicron range. Materials are opaque, with a certain amount of birefringence, more evident in the samples with high hard phase content and expectedly high cristallinity.

SEM on freeze-fractured surfaces clearly showed in many samples the presence of a macrophase separation characterized by dispersed spherical domains immersed in a continuous matrix. Such domains may be well evident as in HFPU1 (Fig. 1), or more hidden as in HFPU2 (Fig. 2), but in all cases very good adhesion between the matrix and the dispersed domains is observed.

Etching the surfaces with dimethyl formamide (DMF), which is a good solvent for hydrogenated chains, but cannot dissolve PFPE chains, allows

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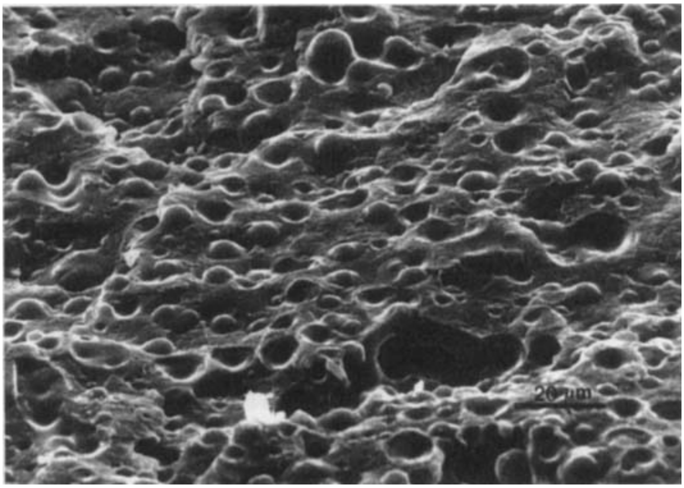

FIGURE 1 SEM micrograph of HFPU1 fracture surface.

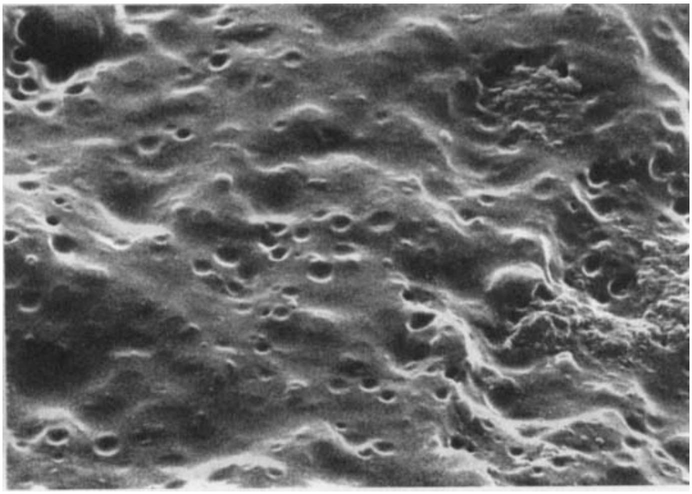

FIGURE 2 SEM micrograph of HFPU2 fracture surface.

the domains to be observed. As shown in Figure 1, the domains are not isolated individual spheres, but, instead, are interconnected by filaments of material of the same chemical nature that, on the basis of the solubility revealed by the etching treatment, is thought to be mainly PFPE blocks. Proof was obtained by X-ray microanalysis. Pointing the probe at positions a, b, c of Figure 3, corresponding respectively to the matrix, a dispersed domain, and an interconnecting filament, the spectra of Figure 4 were obtained. The ratio of the O/F peaks suggests that the fluorinated chains accumulate in the interconnecting material more than in the dispersed domains, whereas they are practically absent in the matrix. From this analysis, it can be deemed that the PFPE blocks tend to self-segregate from the mainly hydrogenated matrix.

To gather further information, TEM was applied. The major problem of TEM of polymers is to have sufficient sample contrast to clearly image all features. To improve the poor mass contrast typical of organic polymers, staining agents based on heavy atoms are customarily used: among them, O_SO_4 and $Ru0_4$ have gained wide popularity as strong oxidants acting on the basis of physical absorption and chemical reaction with the substrate. O_SO_4 is typically used for double bonds, with which quantitatively reacts forming inter- and intramolecular linkages. $Ru0_4$ is a general purpose strong oxidating agent active with a variety of chemi-

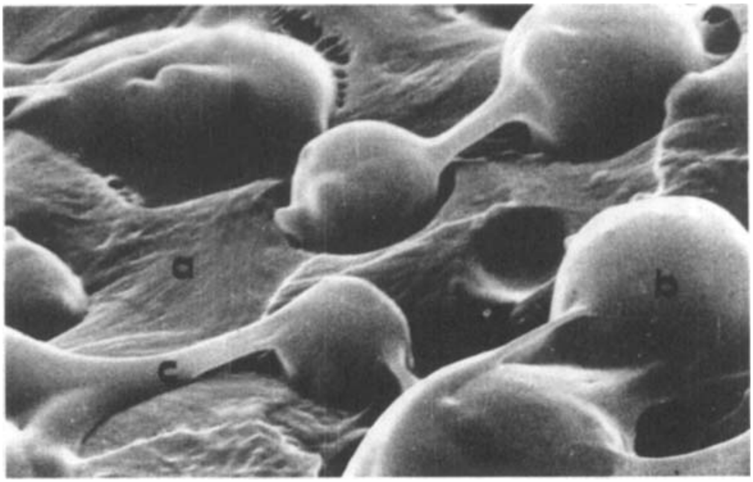

FIGURE 3 SEM micrograph of HFPU1 fracture surface after etching with DMF for 4 h.

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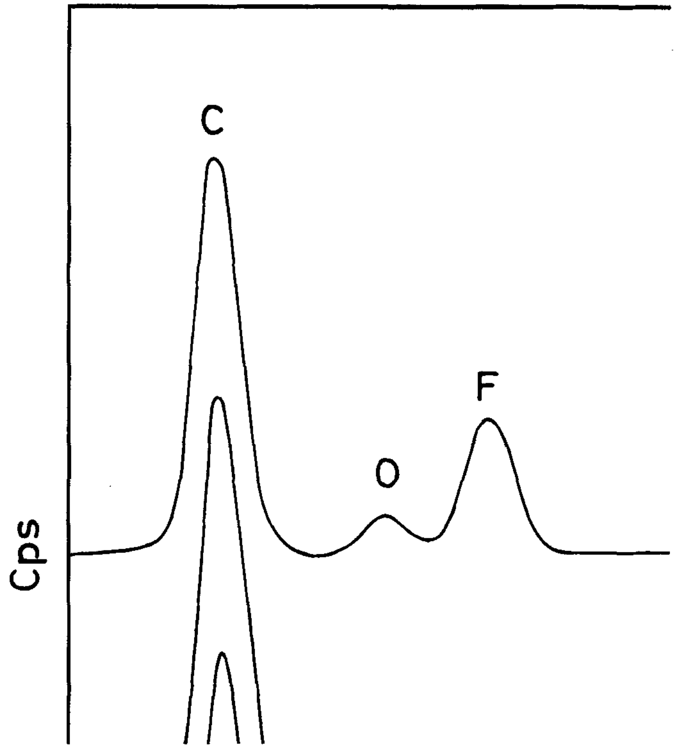

FIGURE 4 X-ray microanalysis of different zones in HFPU1: **a**) matrix; **b**) dispersed domain; **c**) interconnecting material (see also Fig. 3).

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cal groups present in polymers,[14,15] among others the aromatic rings and the ethers.

The presence of aromatic MDI moieties and hydrogenated polyethers and polyesters blocks in the PUs that are reactive with $Ru0_4$, and of PFPE chains that are generally chemically inert, seemed to be a favourable situation for attaining selective staining of the components. In fact, preliminary experiments with liquid PFPE macromers showed that PFPE was unattacked by O_S0_4 and $Ru0_4$, even after several hours of exposure to the vapors.

Both agents were tried with bulk and ultramicrotomed specimens. Two examples are reported in Figure 5a,b. Figure 5a is the TEM micrograph of HFPU2 treated with O_S0_4 in bulk for 48 h and subsequently for 30 min as ultrathin sections. Figure 5b refers to the same material treated for 30 min with $Ru0_4$ only after ultramicrotoming. As expected the treatment with $Ru0_4$ attained a higher contrast and discrimination of finer details, such as the connections between the matrix, heavily stained, and the dispersed domains; these last ones and the filaments connecting some segregated domains remain white because they were unattacked by the staining agent. Moreover the operational times are much shorter in the case of $Ru0_4$. Therefore, all of the following TEM photomicrographs will refer to samples stained with $Ru0_4$.

The effectiveness of Ru staining is best shown in Figure 6 referring to HFPU1 already investigated by SEM (Fig. 1). $Ru0_4$ staining and TEM unambiguously show that the globular domains are actually formed by shell-core structures, in which the shell is formed by perfluorinated chains,

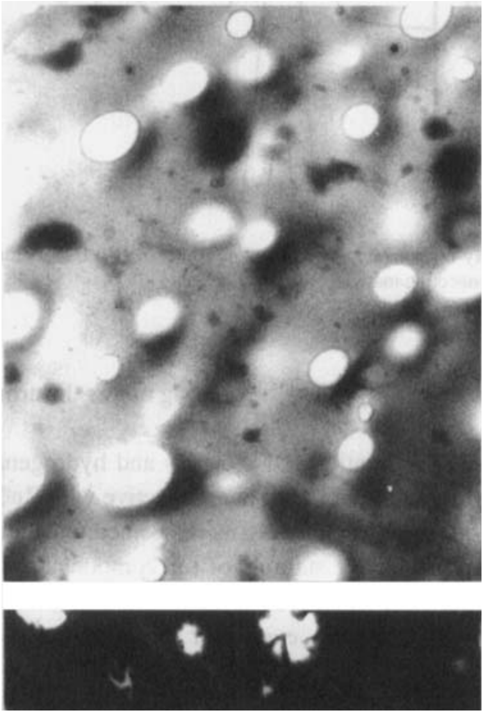

FIGURE 5 TEM micrographs of ultrathin sections of HFPU2 treated with: **a**) O_SO_4; **b**) RuO_4.

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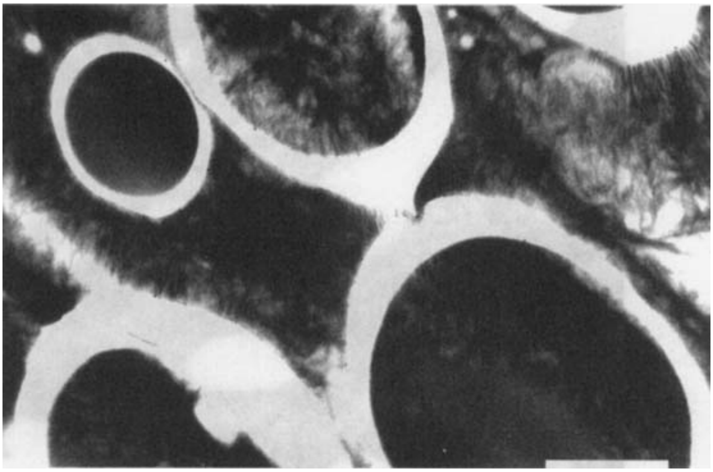

FIGURE 6 TEM micrograph of HFPU1 ultrathin sections stained with RuO_4.

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unstained by RuO_4, whereas the core is mainly composed by hard and soft hydrogenated material similar to the matrix. The shells are often connected through filaments in a semicontinuous network. This result is in good agreement with the microanalysis data on fluorine distribution shown in Figure 4. Moreover, in the cores, lamellae and pseudospherulitic structures are also visible together with more homogeneously stained areas. This might also indicate an uneven distribution of the hard sequences.

The increase of the hard phase content favors the appearance of well-developed crystalline structures: for instance, by increasing the hard-phase content from 22.7% in HFPU5 (Fig. 7) to 32% in HFPU3 (Fig. 8a), the formation of crystalline lamellae, well evidenced in detail in Figure 8b, is favored; in such picture, the resolution was enhanced by filtering the electrons in a TEM equipped with an element-specific imaging (ESI) apparatus. As a consequence, the fluorinated domains, which are white in normal contrast, turn grey.

At high magnification, a microphase separation characterized by very small phase dimensions also is observed, which is usual in segmented polyether-urethanes.[16] Such microphase separation arises from the immiscibility between the hard-(MDI-BDO) and the soft-polyether sequences, that in this case are composed of the hydrogenated polyglycol chains and a few PFPE blocks which did not macrosegregate.

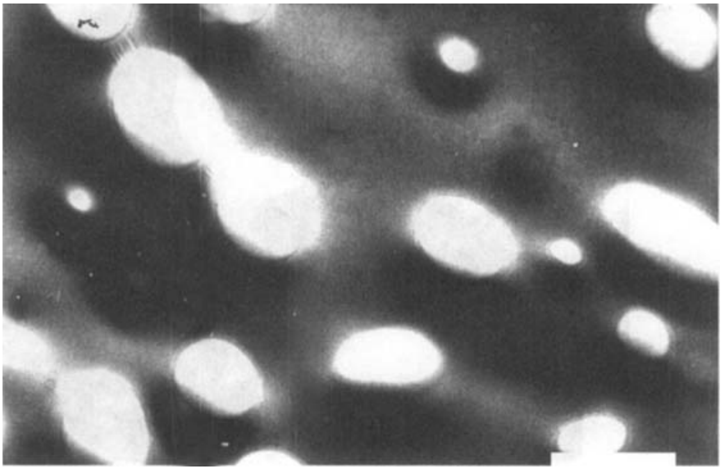

FIGURE 7 TEM micrograph of HFPU5 ultrathin sections stained with $RU0_4$.

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The presence of a microphase separation was also proved by DSC and DMS measurements which show independent glass transitions of two soft phases (PFPE, PTMEG or PCL) and the fusion of the crystalline hard phase. The thermal data will be presented in a future paper.[17]

Finally, Figure 9 shows the morphology of FPU4 containing only a fluorinated soft phase that is the matrix in which black domains of hard phase are finely dispersed. The gray and black areas suggest the presence of copolymer chains with different contents of hard segments.

DISCUSSION

The morphological investigation clearly pointed out some very important features of these PUs containing both PFPE and PTMEG/PCL soft blocks: the coexistence of a micro- and a macro-phase separation.

Whereas the microphase separation is a beneficial feature in sequential polyurethanes, since it dominates the mechanical properties and the behavior of thermoplastic elastomers, the macrophase separation is an unwanted characteristic which may reduce material performance.

The macrophase separation in PU systems was observed and investigated by Thomas, Mc Knight and others[18-21] for polymers made from toluene

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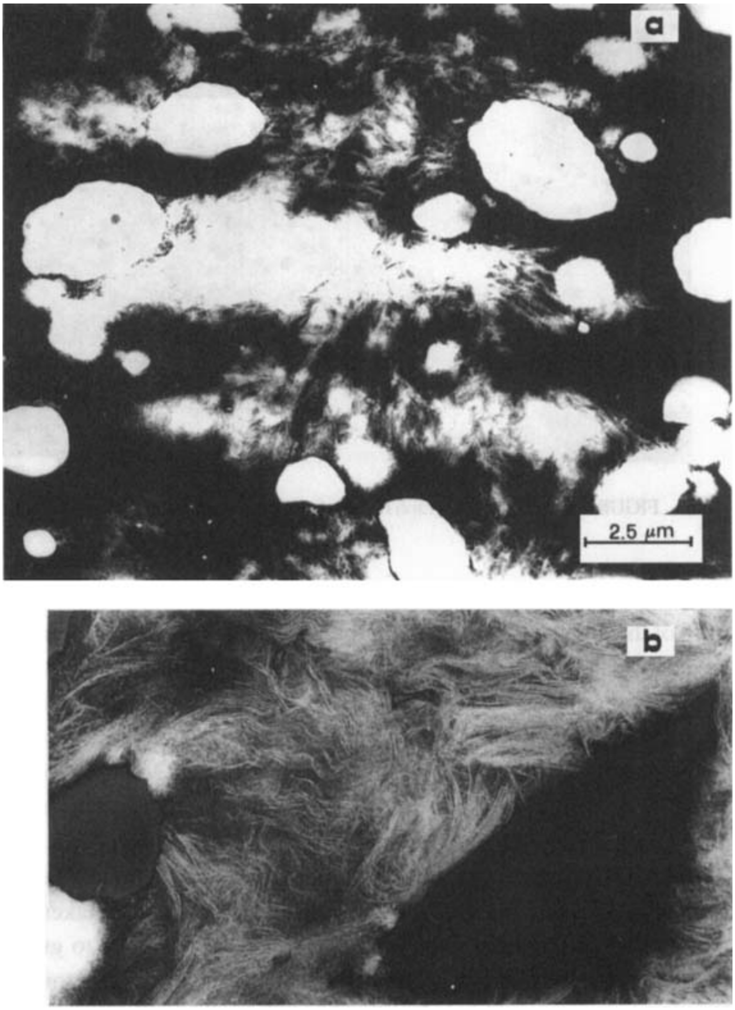

FIGURE 8 TEM micrograph of HFPU3 ultrathin sections stained with RuO_4: **a**) overview; **b**) enlarged detail (filtered image obtained with ESI-TEM).

diisocyanate (TDI), BDO, and hydroxyl-terminated polybutadiene (HTPBD), and was clearly related to the reagents immiscibility during the stage of prepolymer formation. In fact they found that, if the reactants are immiscible and the polycondensation reaction starts in an immiscible heterogeneous system, the composition of the final polymer is controlled by the

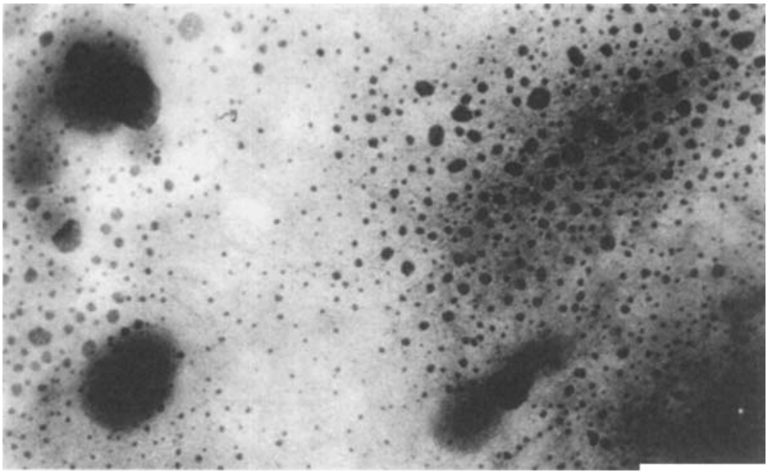

FIGURE 9 TEM micrograph of FPU4 ultrathin sections stained with RuO_4.

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diffusion rate of the species from one phase to another beside by reaction rates of the different functional groups. As a consequence, the composition of the chains is far from the statistical one, obtainable in conventional PU polymerized from miscible monomers in homogeneous phase, thus phases rich in one monomer and poor in the other one are formed and phase separate.

Considering that PFPE is totally immiscible with MDI, as well as with PTMEG or PCL, as it is also evidenced by the solubility parameters ($\delta = 29$, 16.3, 17.3, 19.3, 10.5 $(Jcm^{-3})^{1/2}$ for MDI, BDO, PTMEG, PCL and ZDOLTX®, respectively),[11,22] it is clear that such compositional heterogeneity is present even in our PUs. Despite the precautions taken to ensure maximum PFPE dispersion, part of the PFPE blocks tends to grow within their own droplets through MDI bridges, independently of the stoichiometric ratio in the mixture. This behavior gives rise to long PFPE-rich sequences which segregate as dispersed domains. Such a process probably is not complete and a compositional gradient is present which ensures a good degree of interfacial interaction among the phases, as witnessed by good adhesion. On the other side, MDI-BDO hard sequences, longer than expected are formed: these long, hard segments can crystallize during the slow cooling, annealing treatment, forming stable crystals with high melting points. This explains the presence of visible lamellae and spherulites which are common features in crystalline PUs but usually appear for a higher average hard-phase content.

It can be concluded that the immiscibility of the reagents during the prepolymerization and the chain extension steps lead to the formation of chains with very different composition that segregate in separate phases. The morphology is complex and different from one PU to another of different composition, being a subtle balance of miscibility, rate of reaction and diffusion, influenced by temperature, time and fluidity of the reagent liquid.

It may be worth noting that direct analytical evidence of different chain compositions are difficult to find since these PU samples cannot be dissolved in common chromatographic solvents; however, further efforts in this direction are being made.

CONCLUSIONS

In the present work, we established a methodology for the morphological analysis of a new class of thermoplastic PU elastomers containing PFPE blocks never before investigated. It was shown that PFPE blocks are inert to the oxidation by $Ru0_4$ which selectively attacks nonfluorinated amorphous and crystalline phases. The TEM of $Ru0_4$-stained ultrasections is the most efficient way of investigating the phase morphology which is characterized by a micro- and a macrophase separation.

The macrophase separation is related to the immiscibility of the reagents, namely of PFPE macromers with MDI and PTMEG or PCL.

The polycondensation in bulk, although operated by a multistep procedure aimed to counteract the tendency of PFPE to homopolymerize, leads to a nonstatistical distribution of soft and hard blocks and to heterogeneous materials. Such compositional heterogeneity and the related phase macroseparation would indicate a material behavior closer to that of polymer blends, than to a sequential, random block copolymer.

To overcome this drawback new synthetic routes should be designed. Preliminary attempts of improving the random dispersion of PFPE blocks in the soft phase by operating in solution with carefully controlled stoichiometry and purity in each step did lead to successful results, as evidenced by the optical clarity of the material and homogeneous morphology.[17]

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