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THE MORPHOLOGY AND STRUCTURE OF POLYACETYLENE-POLYBUTADIENE GRAFT COPOLYMER FILMS °

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Abstract The morphology and the structure of a new PA copolymer has been investigated by means of TEM,WAXS and ED techniques.Crystalline PA microdomains,less than 100 Å in size,aggregate preferentially into ca.2000 Å long and ca.400 Å wide worm like morphological units,in their turn embedded in a PA poor PB matrix.

PA copolymers and blends are receiving considerable attention owing to their favourable properties with the respect to the omopolymer, namely greater air stability,better processability and comparable conductivity [1-3].However the morphology and structure of these materials together with their influence in affecting the above citated properties,are up to now a quite controversial issue.Therefore we have investigated by means of the TEM,ED,WAXS techniques,thin and thick films of a new copolymer obtained by grafting PA onto 1,4 cis polybutadiene (PB) [4]. Samples were prepared from appropriately diluted reaction solution according the following procedure:-room and low (-20 °C) temperature evaporation to obtain thin (≪2000 Å) and thick films (40μ thickness)on water,carbon film or glass;-room temperature evaporation on Mylar film,subsequent stretching to get oriented films. The PA content in the samples was 10,20,35,50 %,the cis/trans ratio being 70/30,30/70,20/80,10/90.The observations were

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carried out on as cast thin films or on thin sections obtained by ultramicrotomy at room or low (-120 °C) temperatures.Where required films were stained with OsO_4 vapours which react both with PB and PA polymers,but are not able to penetrate crystalline PA regions so that in the pictures PA microdomains appear brighter.TEM,ED experiments were performed on Siemens Elmiscope 102 and on Joel 200 B STEM microscopes.

WAXS and ED studies indicates that the copolymer is constituted by amorphous PB and PA predominantly crystallized in a cis or trans modification already described [5].Depending on the reaction conditions upon stretching (up to 4X) PA chains tend to allign along the elongation direction. In the fiber pattern no layer lines were detected. The degree of elongation and orientation attainable by PA chains increase on decreasing the PA content in the film.The azimutal breadth of the strongest equatorial reflections ranges from 45° to 20° approximately for 50% and 25% PA content in the copolymer respectively. Line broadening evaluation indicates that the coherent PA microdomains average less than 100 Å in size,normally to the chain direction. In all differently prepared samples a clear partial segregation is observed:polydispersed worm-like PA-rich morphological units are embedded into a PB rich amorphous matrix. The population density of this units depends on PA content (see Fig.1A and 1B). Cis PA rich films do not exhibit any noteworthy difference in morphology,whereas the shape regularity of the aggregates appears to be enhanced in low temperature slowly evaporated films. The average dimensions of the worm-like units (aggregates) consistently range from 1000 to 4000 Å in length and from 100 to 500 Å in diameter, probably depending on copolymer molecular weight dispersion. Micrographs obtained from ultramicrotomed thick films indicate that the PA rich aggregates are,in their turns,constituted by randomly distributed microdomains of 60-80 Å in diameter (see Fig.2A).

Microdomains subunits of comparable size can also be observed in appropriate solvent cast films,both unstained and OsO_4 vapour treated

(see Fig.2B).

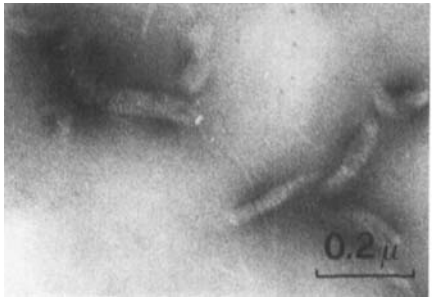

FIG.1A

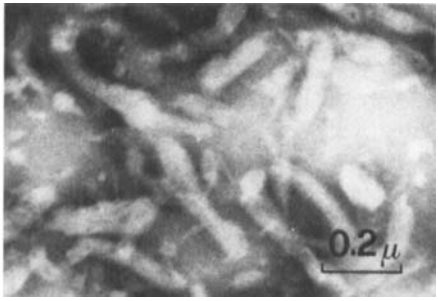

FIG.1B

OsO_4 stained samples with increased PA content:10% 1A,50% 1B

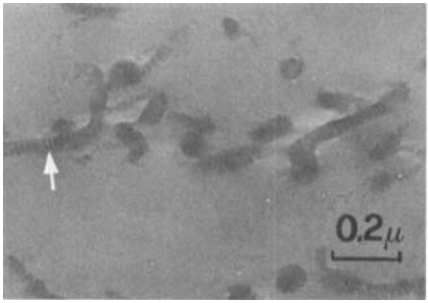

FIG.2A

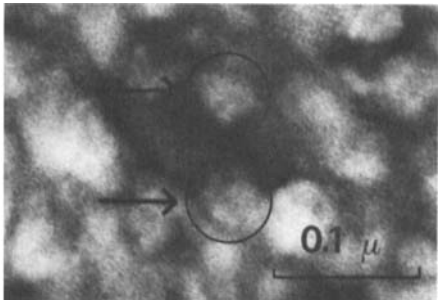

FIG.2B

Isolated aggregates showing the hyperfine morphology:2A as cast;2B normally ultramicrotomed.

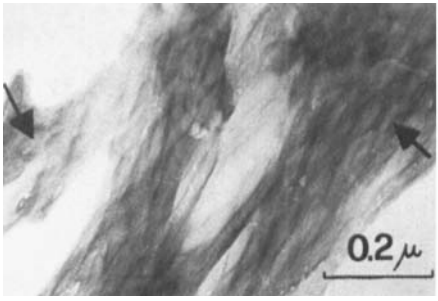

FIG.3A

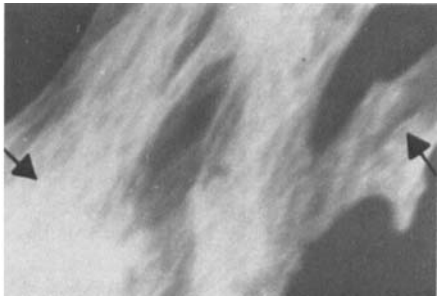

FIG.3B

Stretched films in bright (3A) and dark (3B) field

These subunits are packed in the worm-like aggregates,but are also observable in the PB rich matrix,although in a much lower concentration. This hyperfine morphology is consistent with WAXS and ED studies. Selected area (5000 $Å^2$) and observations on isolated worm-like structure appear to be consistent with a complete randomness of PA crystallite orientation.Laser Raman studies on copolymer solution[6] together with UV-visible spectra on films indicate an average conjugation length of 25 double bonds approximately (i.e. 65 Å) which seems to correlate reasonably with the size of the coherently scattering microdomains. Both in films elongated on Mylar and in electron beam damaged films,which frequently stretch or fail locally, the worm-like aggregates tend to align along the elongation direction as shown in bright (see Fig.3A) and dark (see Fig.3B) field images. Selected areas ED (5000 $Å^2$) do not indicate any preferential orientation of PA chains:the observed pattern are identical to those of the unstretched samples.In dark field micrographs of the sample elongated in the electron beam the presence of a fibrillar morphology,which is not observable in the corresponding bright field,nor in any micrographs of the unstretched copolymer,cannot be ruled out. In conclusion our observations are consistent with a morphology neither fibrillar nor fully polydispersed[3].Our findings can be interpreted in terms of a three phase system,namely:1-crystalline PA microdomains mainly aggregated into worm-like superstructures;2-PA-PB amorphous regions,intercalating type-1 domains in the worm-like structure,but also present in type -3 regions;3-PB amorphous matrix.

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