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MODEL BLOCK COPOLYMERS WITH COMPLEX ARCHITECTURE

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Abstract: The synthesis of non linear block copolymers of the type $(BA)_2B$ (3-miktoarm star copolymer), $(BA)_3B$ (4-miktoarm star copolymer), $(BA)_3B(AB)_3$ (super H-shaped), B_2AB_2 (H-shaped) and (B,A)A(B,A) (π-shaped), where A is polyisoprene 1,4 and B is polystyrene was performed using anionic polymerization techniques and suitable chlorosilane chemistry. Characterization data showed that the samples are molecularly and compositionally homogeneous. TEM, SAXS and SANS were used to study the microphase behavior of the copolymers. For all samples, the results were analyzed in the frame of the theoretical predictions given by Milner and taking into account the results from previous studies on the A_2B and A_3B miktoarm star copolymers.

INTRODUCTION

Recent advances in anionic polymerization have allowed the preparation of novel well-defined block copolymer architectures. These new structures are of great academic and industrial interest, since on the one hand they can be used as model compounds for establishing the relationship between structure and properties and on the other hand they have the potential of multiple applications.

Until now the most convenient method for the control of the macromolecular architecture is the chlorosilane approach, ie. the linking living polymer chains to multifunctional chlorosilane compounds. Using this method model miktoarm stars (from the greek word μικτός meaning mixed) of the following structures were prepared: A_2B, A_3B, A_5B, A_2C_2, $(AB)_2(BA)_2$, ABC and ABCD, were A, B and C, are polyisoprene-1,4 (PI), polystyrene (PS), or polybutadiene-1,4 (PB) and D is poly(4-methylstyrene)$^{1-6)}$. More complex structures of the type A_2BA_2 (H-shaped copolymers)

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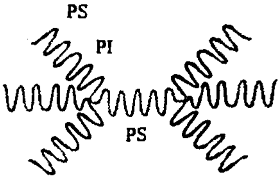
and A_3BA_3 (super H-shaped copolymers) were also prepared using sodium naphthalenide as a difunctional initiator and suitable chlorosilane chemistry[7].

The microphase separation behavior of these copolymers was studied in the frame of the recent theoretical developments concerning the phase behavior of block copolymers and the influence of their structure to the equilibrium morphology[8-12]. The most important conclusion extracted from these studies is that the architecture can alter dramatically the morphology compared with linear block copolymers.

In this communication we are reviewing the synthesis of novel block copolymers of the following structure: $(BA)_2B$ (3-miktoarm star copolymer), $(BA)_3B$ (4-miktoarm star copolymer), $(BA)_3B(AB)_3$ (super H-shaped)[13], B_2AB_2 (H-shaped)[14,15] and (B,A)A(B,A) (π-shaped)[16] as shown in fig. 1. We are also summarizing the equilibrium morphology at the strong segregation limit (SSL) as investigated by transmission electron microscopy (TEM), small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS).

3-miktoarm star copolymer

4-miktoarm star copolymer



super H-shaped copolymer

H-shaped copolymer

π-shaped copolymer

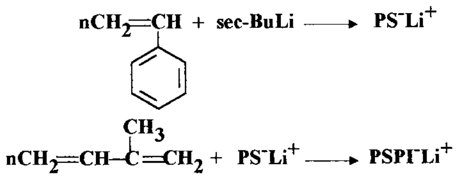
Fig. 1: Several block copolymers with complex architectures

RESULTS AND DISCUSSION

A. Synthesis and Characterization

$(BA)_2B$ and $(BA)_3B$ 3- and 4-miktoarm star copolymers

The synthesis of the 3-miktoarm star copolymers, based on the protocol used for the synthesis of the A_2B miktoarm stars[3)], was achieved by the following reaction series:



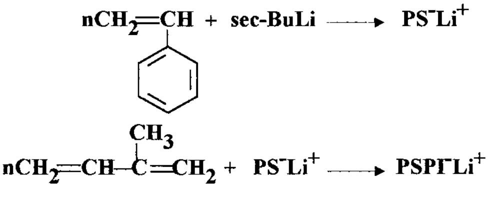
$$PS^-Li^+ + (\text{excess})\ (CH_3)SiCl_3 \longrightarrow PSSi(CH_3)Cl_2 + LiCl + (CH_3)SiCl_3\uparrow$$

$$(\text{small excess})\quad PSPI^-Li^+ + PSSi(CH_3)Cl_2 \longrightarrow PS(PIPS)_2Si(CH_3) + 2LiCl$$

3-miktoarm star

The method is based on the reaction of the living B arm with the excess methyltrichlorosilane, followed by the evaporation of the excess silane and the final linking of the living diblock chains BA to the dichlorosilane macromolecular linking agent.

A similar procedure was performed for the synthesis of the $(BA)_3B$ 4-miktoarm star copolymers except that tetrachlorosilane was used as the linking agent. The reaction sequence is outlined as follows:



$$PS^-Li^+ + (\text{excess})\ SiCl_4 \longrightarrow PSSiCl_3 + LiCl + SiCl_4\uparrow$$

$$(\text{small excess})\quad PSPI^-Li^+ + PSSiCl_3 \longrightarrow PS(PIPS)_3Si + 3LiCl$$

4 miktoarm star

The molecular and compositional characterization data of the miktoarm star copolymers prepared are given in Tab. 1.

Tab. 1. *Molecular characteristics of 3- and 4-miktoarm star copolymers of the $(BA)_2B$ and $(BA)_3B$ type.*

	$M_n \times 10^{-3}$ a)			M_w	I c)	wt, -%PS	wt, -%PS	wt, -%PS
Sample	PS	PSI	Star	x 10^{-3} b) Star	Star	UV-SEC	^{1}H-NMR	calc.
$(PSI)_2PS$	21.5	51.4	129.0	133.5	1.05	51	50	52
$(PSI)_3PS$	21.5	51.4	185.0	193.2	1.05	49	48	49

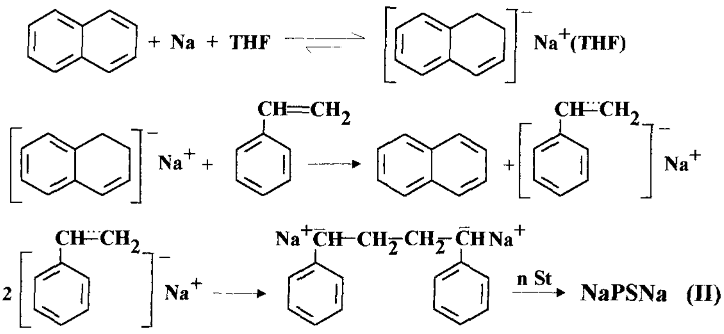
a) Membrane osmometry (MO) in toluene at 35° C.

b) Low angle laser light scattering (LALLS) in THF at 25° C.

c) Size exclusion chromatography (SEC) in THF at 30° C.

$(BA)_3B(AB)_3$ Super H-shaped block copolymer

The reaction sequence used for the preparation of the super H-shaped block copolymer is given below:



$$\mathbf{(II) + (excess)\ SiCl_4 \longrightarrow Cl_3SiPSSiCl_3\ (III) + 2NaCl + SiCl_4\uparrow}$$

$$\mathbf{n\ Styrene + sec\text{-}BuLi \longrightarrow PS^-Li^+\ (A)}$$

$$\mathbf{n\ Isoprene + PS^-Li^+ \longrightarrow PSPI^-Li^+\ (AB)}$$

$$\mathbf{(III) + (excess)\ PSPI^-Li^+ \longrightarrow (PSPI)_3PS(PIPS)_3 + 6LiCl}$$

Super H-shaped
block copolymer

The method that was followed was similar with the one adopted previously for the preparation of the A_3BA_3 type super H-shaped block copolymers[7)]. It involved the polymerization of styrene with sodium naphthalenide acting as a difunctional initiator and the subsequent reaction of the living polymer with excess tetrachlorosilane. After the excess silane was removed living BA chains were added to the macromolecular linking agent for the preparation of the super H-shaped block copolymer. It's molecular and compositional characteristics are given in Tab. 2.

Tab. 2. *Molecular characteristics of the $(BA)_3B(AB)_3$ Super H-shaped block copolymer.*

	$M_n \times 10^{-3}$ a)				M_w	I c)	wt, -%PS	wt, -%PS	wt, -%PS
Sample	PS connector	PS	PSI	Star	$\times 10^{-3}$ b) Star	Star	UV-SEC	^{1}H-NMR	calc.
Super H	46.0	21.5	51.4	315.2	337.3	1.09	49	48	49

a) Membrane osmometry (MO) in toluene at 35° C.

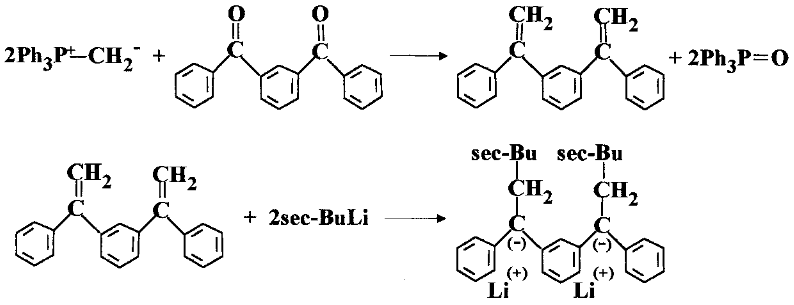
b) Low angle laser light scattering (LALLS) in THF at 25° C.

c) Size exclusion chromatography (SEC) in THF at 30° C.

B_2AB_2 H-shaped and $(B,A)A(B,A)$ π-shaped block copolymers.

The reaction sequence for the preparation of the B_2AB_2 H-shaped block copolymers is outlined below:

$$Ph_3P^+CH_3I^- + CH_3Li \longrightarrow [Ph_3P^+\!-CH_2^- \longleftrightarrow Ph_3P{=}CH_2] + CH_4 + LiI$$



DLI

$$\text{Styrene} + sec\text{-BuLi} \xrightarrow{\text{Benzene}} \text{PSLi}$$

$$2\text{PSLi} + \text{CH}_3\text{SiCl}_3 \xrightarrow{\text{Benzene}} (\text{PS})_2\text{SiCH}_3\text{Cl} + 2\text{LiCl}$$

$$\text{Isoprene} + \text{DLI} \xrightarrow[sec\text{-BuOLi}]{\text{Benzene}} \text{LiPILi}$$

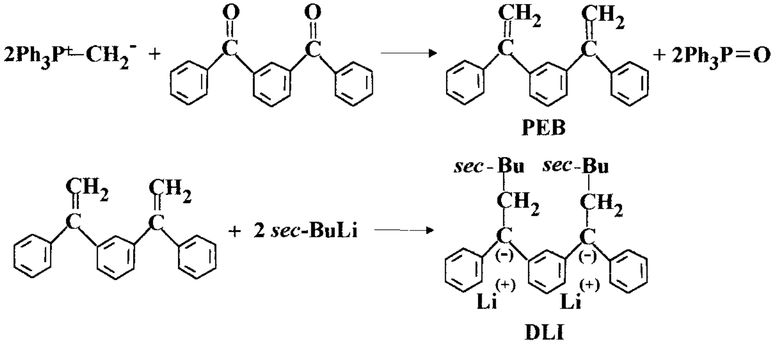
$$\text{LiPILi} + \text{excess}(\text{PS})_2\text{SiCH}_3\text{Cl} \xrightarrow[\text{THF (trace)}]{\text{Benzene}} (\text{PS})_2(\text{CH}_3)\text{SiPISi}(\text{CH}_3)(\text{PS})_2 + 2\text{LiCl}$$

$(\text{PS})_2\text{PI}(\text{PS})_2$ or H-shaped copolymer

The difunctional initiator was prepared by the addition of sec-BuLi to 1,3-bis(1-phenylethenyl)benzene (PEB)17). Isoprene was polymerized with this initiator in benzene to produce the difunctional living polyisoprene 1,4. In another reactor living polystyryllithium was added to a methyltrichlorosilane solution in a Li/Cl ratio 2.1/3. Steric hindrance effects of the living polymer chains ensure the formation of only the coupled product. Finally the living difunctional polymer was reacted with a small excess of the macromolecular linking agent to produce the H-shaped copolymer. The synthetic strategy was analogous to the one developed by Roovers and Toporowski for the synthesis of H-shaped PS homopolymers18). The molecular and compositional characteristics of these copolymers are given in Tab. 3.

A similar procedure was used for the preparation of the (B,A)A(B,A) π-shaped block copolymers, as shown by the following reaction scheme:

$$\text{Ph}_3\text{P}^+\text{CH}_3\text{I}^- + \text{CH}_3\text{Li} \longrightarrow [\text{Ph}_3\text{P}^+\text{–CH}_2^- \longleftrightarrow \text{Ph}_3\text{P=CH}_2] + \text{CH}_4 + \text{LiI}$$



Tab. 3. *Molecular characteristics of the H-shaped copolymers*

Sample	M_n[a] arm PS x10^{-3}	M_n[a] con PI x10^{-3}	M_n[a] H x10^{-3}	M_w[b] H x10^{-3}	(M_w/M_n)[c] H	(dn/dc)[d] H	wt,- %PS ^{1}H-NMR	wt,- %PS UV-SEC	wt,- %PS calcul.
H_1	52.2	22.1	228.4	246.7	1.08	0.182	90.0	92.2	91.4
H_2	47.5	37.7	226.5	242.4	1.07	0.180	84.2	84.7	83.9
H_3	31.3	108.1	239.8	254.2	1.06	0.160	51.1	52.8	52.2
H_4	18.3	159.9	245.4	262.6	1.07	0.145	28.6	29.6	29.8
H_5	15.0	171.3	237.8	254.4	1.07	0.142	24.6	27.0	25.2
H_6	8.4[e]	194.2	235.2	256.4	1.09	0.135	13.5	15.2	14.3
H_7	3.5[e]	258.9	286.6	303.8	1.06	0.130	4.2	5.0	4.9

[a] Membrane Osmometry (MO) in toluene at 35°C.

[b] Low Angle Laser Light Scattering (LALLS) in THF at 25°C.

[c] Size Exclusion Chromatography (SEC) in THF at 30°C.

[d] Laser Differential Refractometry in THF at 25°C, (dn/dc) in mLg^{-1}.

[e] Vapor Pressure Osmometry (VPO) in toluene at 50°C.

$$\text{Isoprene} + sec\text{-BuLi} \xrightarrow{\text{benzene}} \text{PILi}$$

$$\text{PILi} + (\text{excess})\text{CH}_3\text{SiCl}_3 \xrightarrow{\text{benzene}} \text{PISiCH}_3\text{Cl}_2 + \text{LiCl} + \text{CH}_3\text{SiCl}_3\uparrow$$

$$\text{Styrene} + sec\text{-BuLi} \xrightarrow{\text{benzene}} \text{PSLi}$$

$$\text{PSLi} + \text{PISiCH}_3\text{Cl}_2 \xrightarrow{\text{benzene}} (\text{PS})(\text{PI})\text{SiCH}_3\text{Cl} + \text{LiCl}$$

$$\text{Is} + \text{DLI} \xrightarrow[sec\text{-BuOLi}]{\text{benzene}} \text{LiPILi}$$

$$\text{LiPILi} + (\text{excess})(\text{PS})(\text{PI})\text{SiCH}_3\text{Cl} \xrightarrow[\text{THF(trace)}]{\text{benzene}} (\text{PS})(\text{PI})(\text{CH}_3)\text{SiPISi}(\text{CH}_3)(\text{PI})(\text{PS}) + 2\text{LiCl}$$

(PS,PI)PI(PI,PS) or π-shaped copolymer

The difference in the synthesis of the π-shaped compared to the H-shaped copolymers is the step of the preparation of the macromolecular linking agent. In the former case the living PI chains reacted with an excess methyltrichlorosilane for the formation of the dichlorosilane end-capped polymer. This was followed by a slow addition of the living PS chains for the formation of the monofunctional linking agent, which was then reacted with the living difunctional PI chains. Characteristic SEC chromatograms from the synthesis of one of the H-shaped copolymers are given in fig. 2.

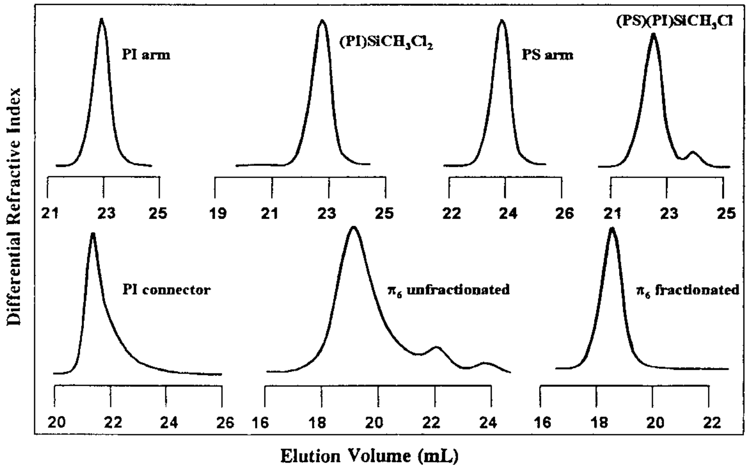


Fig. 2: SEC chromatograms of the PS and the PI arms, the products of the linking reactions (PI)SiCH$_3$Cl$_2$ and (PS)(PI)SiCH$_3$Cl, the difunctional connector and the π$_6$-shaped copolymer, before and after fractionation.

The data concerning the molecular and compositional characterization of the π-shaped copolymers are given in Tab. 4.

B. Morphology

The microphase separation behavior of miktoarm star copolymers of the type A_2B and A_3B was extensively studied experimentally[3,5)] in the frame of the theoretical predictions given by Milner[9)]. The proposed phase diagram in the strong segregation limit, shown in fig. 3, clearly indicates that the star architecture influences dramatically the equilibrium morphology. The experimental results confirm Milner's predictions indicating, however that for $\varepsilon \sim 2$ or higher the theory slightly overestimates the shift in the volume fraction ranges, where ε is the packing length.

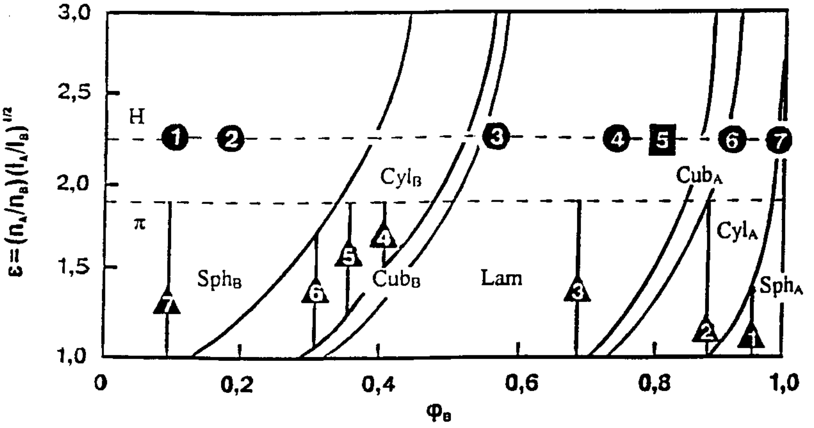


Fig.3: Theoretical phase diagram calculated by Milner. In this diagram A is PI and B is PS. The position of the H- and π-shaped copolymers is also shown.

TEM and SAXS results on the 3- and 4-miktoarm star copolymers $(PS\text{-}b\text{-}PI)_nPS$, where n=2,3 and the super H-shaped block copolymer showed that all samples form alternating lamellae at a PS volume fraction in the range 0.51-0.56. It is evident that the exhibited morphology cannot be obtained by the Milner diagram for A_2B and A_3B miktoarm stars, because in the former case the A arms are not single

Tab. 4. *Molecular characteristics of the π-shaped copolymers*

Sample	$M_n^{a)}$ arm PI x10^{-3}	$M_n^{a)}$ arm PS x10^{-3}	$M_n^{a)}$ con. PI x10^{-3}	$M_n^{a)}$ π x10^{-3}	$M_w^{b)}$ π x10^{-3}	$(M_w/M_n)^{c)}$ π	$(dn/dc)^{d)}$ π	wt,- %PS ^{1}H NMR	wt,- %PS UV-SEC	wt,- %PS calcul.
π_1	4.9$^{e)}$	109.0	3.9$^{e)}$	230.8	244.6	1.06	0.184	94.9	94.8	94.5
π_2	8.9$^{e)}$	92.1	11.1$^{e)}$	212.4	225.1	1.06	0.181	88.9	89.7	86.7
π_3	20.5	70.9	17.1	200.3	214.3	1.07	0.171	71.3	71.8	70.8
π_4	39.4	48.1	50.0	220.3	235.7	1.07	0.154	43.1	44.4	43.7
π_5	37.8	34.6	42.3	180.7	195.2	1.08	0.149	37.7	38.3	38.3
π_6	45.2	34.3	56.0	211.8	226.6	1.07	0.145	31.1	33.2	32.4
π_7	65.5	10.8$^{e)}$	71.7	235.1	258.6	1.10	0.132	8.6	9.9	9.2

a) Membrane Osmometry (MO) in toluene at 35°C.
b) Low Angle Laser Light Scattering (LALLS) in THF at 25°C.
c) Size Exclusion Chromatography (SEC) in THF at 30°C.
d) Laser Differential Refractometry in THF at 25°C, (dn/dc) in mLg^{-1}.
e) Vapor Pressure Osmometry (VPO) in toluene at 50°C.

chains but they are consisting by block copolymers, thus leading to increased number of junctions for these molecules and specially for the super H-shaped copolymer. It is better to consider these stars as a combination of di- and triblocks. Binary blends with PS and PI homopolymers were also prepared19). The lamellar morphology was maintained for overall volume fraction of PS up to 0.69, where a transition to cylindrical microdomains was occurred without the observation of an intervening cubic structure, a behavior similar to that of diblocks. A lamellae-catenoid morphology was found from the blends of the super H-shaped copolymers. This phase was observed only for blends of diblocks with homopolymers20) in the past and it is the first time this behavior was appeared for such a complex structure.

An effort was made to find a method by which Milner's diagram can be applied to explain the phase behavior of the H-shaped copolymers. In order to adopt this methodology the H architecture was divided into two components which are miktoarm copolymers of the A_2B type, having the same composition as the H-shaped copolymer. It can be considered that the morphology of the H-shaped copolymer is similar to it's constituting A_2B copolymers. The results found were consistent with the predictions of the theory with only two exceptions. These two deviations from the theory indicate that the boundaries of the phase diagram are overestimated, ie. the transition lines should be bent back toward the low PI volume fraction side of the diagram, as was also observed in previous studies5,21).

The inconsistencies between the experiment and the theory can be attributed to the fact that the theory assumes the condition of infinitely strong segregation or in other words infinitely high molar mass and to the fact that the structures are approximated as brushes of blocks, representing the arms of the stars, grafted with equal spacing on the interface. However the miktoarm stars have only one junction point, something that was not considered by Milner. Joining multiple branches to a single junction point facilitates the stretching of the chains on the same side of the interface, compared with the stretching produced when the branches emanate from different junction points of the interface.

Using the same methodology the π architecture is divided to asymmetric miktoarm star copolymers, which are structures with the PI block grafted at the 1/3 of the total PS chain length. However it has to be mentioned that the theoretical calculations were made considering that the blocks of the same type have the same molar mass, or in other words the model was proposed for symmetric miktoarm stars of the type A_nB_m. Practically the problem is focused in the determination of the ε parameter, by which it will be possible to correlate the experiment with the theoretical predictions. The following generalized equation can be used to describe the case of both symmetric and asymmetric miktoarm stars:

$$\varepsilon=f(\tau)(l_a/l_b)^{1/2}$$

where, l_a and l_b are the packing lengths of arms A and B respectively and τ is the A chain length fraction to which the B arm is grafted. When τ=0 or 1 then ε corresponds to the linear diblock behavior: $\varepsilon=(l_a/l_b)^{1/2}$, whereas for τ=0.5 ε represents the A_2B miktoarm star case: $\varepsilon=2(l_a/l_b)^{1/2}$. Consequently between τ=0 and 0.5 the ε value varies continuously in the range between $(l_a/l_b)^{1/2}$ and $2(l_a/l_b)^{1/2}$. The function of ε vs τ must be continuous with a maximum at τ=0.5.

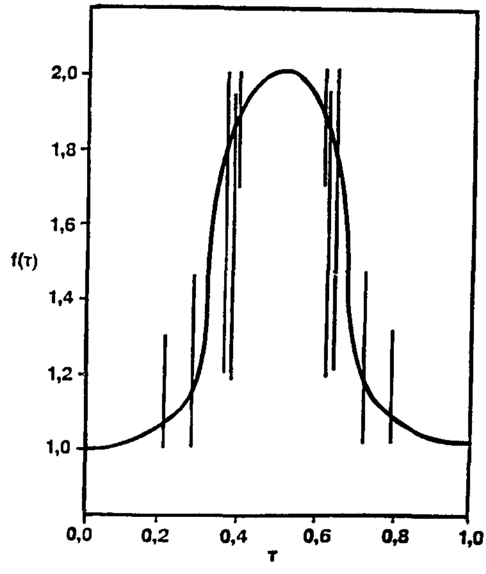


Fig.4: Schematic representation of the function f(τ)

Having these thoughts in mind and the experimental results of the π-shaped copolymers an effort was made to reach some conclusions concerning the relationship between f(τ) and τ. The positions of the π-shaped copolymers in Milner's diagram are given in fig. 3. Using the composition of the samples, the general limits between which

ε varies and assuming that the model is valid for all samples a vertical line for each copolymer was drawn. These lines represent the acceptable range of ε values for each sample. Every copolymer corresponds to an asymmetric miktoarm star with a different τ value. So it is possible to correlate ε and consequently $f(\tau)$ with τ, meaning that for every τ value $f(\tau)$ lies in a specific range of values. All these results can be presented in the diagram of fig. 4, where the function $f(\tau)$ is plotted over τ. It is evident that the function changes slope between τ=0.30 and 0.35. At τ values close to 0 the system behaves like a linear diblock copolymer and by increasing τ the behavior resembles that of the A_2B stars, meaning that the asymmetric stars have a behavior somewhere between the AB linear and the A_2B star copolymers. This is reasonable since the gradual increase of the length of the second A chain makes the crowding effect of both A chains at the same side of the interface more intense, leading to a behavior similar to that obtained by the A_2B stars. However more data are necessary in order to extract the final form of the function $f(\tau)$.

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