PEG 400/Paraffin Oil Non-Aqueous Emulsions Stabilized by PBut-*Block*-P2VP Block Copolymers

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ABSTRACT: For the preparation of PEG 400 in paraffin oil non-aqueous biocompatible emulsions, the stabilization efficiency was compared for two well-defined poly(butadiene)-*block*-poly(2-vinylpyridine) (PBut-*block*-P2VP) block copolymers, with similar molecular weights but different compositions. The PBut$_{128}$-*block*-P2VP$_{50}$ and PBut$_{189}$-*block*-P2VP$_{37}$ samples, designated as copolymer **A** and **B,** respectively, are self-organized in paraffin oil as micelles with a P2VP core and a PBut corona. The PEG 400/paraffin oil emulsion characteristics were determined as a function of the copolymers concentrations and phase ratios. Higher static and shear stabilities were obtained for emulsions stabilized by copolymer **B** than for those obtained in the presence of copolymer **A**. A further difference concerns the droplet size, relative viscosity, and loss modulus values obtained at a given dispersed phase volume fraction. At constant copolymer concentrations, it appeared that copolymer **B**, with a longer PBut sequence, is a more efficient emulsifier and stabilizer than copolymer **A**. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2015**, *132*, 41390.

INTRODUCTION

Non-aqueous or anhydrous emulsions with their application possibilities have been described in several recent review articles.[1–3] An almost exclusively steric stabilization was provided for these emulsions and different authors have demonstrated that polymeric surfactants, such as block or graft copolymers, are more efficient stabilizers than low molecular weight surfactants.[4,5]

Non-aqueous emulsions allow not only to perform a large range of water sensitive reactions, as outlined by Crespy and Landfester,[3] but also to encapsulate hydrolytically unstable drugs for biomedical and cosmetic applications.[6–9] Of particular interest are, therefore, anhydrous emulsions comprising biocompatible block copolymers and oil components such as paraffin oil, ethylene glycols, silicon, and triglyceride oils.[10–15] In view of their topical application, we recently prepared drug-loaded non-aqueous emulsions, with a PEG 400 dispersed phase in a Miglyol 812 continuous phase, stabilized by a poly(butadiene)-*block*-poly(2-vinylpyridine) (PBut-*block*-P2VP) block copolymer.[13]

In this context, the goal of this investigation was to extend the concept of these block copolymers stabilized biocompatible emulsions for the system PEG 400/paraffin oil. To the best of our knowledge only Ramanathan et al.[10] have described a somehow similar system, such as ethylene glycol/paraffin oil stabilized by a poly(butadiene)-*block*-poly(ethylene oxide) (PBut-PEO), for the preparation of polyurethane microspheres. However, the PEO crystallization may induce a decrease of the stabilization efficiency, as outlined by Riess et al.,[16] and, therefore, P2VP-based block copolymers were selected for this study.

It was reported that paraffin oil, is widely used in cosmetic and biomedical formulations. In fact, this oil is an effective and safe moisturizer having an immediate and prolonged lubricating effect as it penetrates into the upper skin layers.[17,18] Another advantage of this type of oil it is its use as base oil for lubricant oil formulations.[19]

PEG 400 is considered as being one of the safest organic solvent for pharmaceutical and cosmetic formulations.[20] Moreover, it facilitates the solubilization and the diffusion of the hydrophobic drugs.[21]

The first aim of this contribution was to examine the micellization of PBut-*block*-P2VP copolymers in paraffin oil, a topic which up to now was only reported by our group[13,14] and by Walther et al.[22] These authors studied the self-aggregation of PBut-*block*-P2VP copolymers in dioxane-water mixtures as a

Additional Supporting Information may be found in the online version of this article.

Table I. Z-average, D_v, and PDI Obtained for PBut-*Block*-P2VP Copolymer Samples at 20 and 30°C

Cop	A				B			
T (°C)	20		30		20		30	
[Cop] (wt %)	0.83	3.33	0.83	3.33	0.83	3.33	0.83	3.33
Z-average (nm)	127.1	130.4	137.0	136.1	47.2	46.7	55.2	60.1
D_v (nm)	128.0	140.0	135.0	137.3	46.6	46.4	54.4	58.6
PDI	0.19	0.23	0.20	0.21	0.15	0.19	0.10	0.20

selective solvent for the P2VP sequence. The formation of spherical micelles with a PBut insoluble core and a P2VP soluble shell could be demonstrated. However, to the best of our knowledge, the "reverse micelles," having a P2VP core and a PBut corona in an aliphatic solvent, such as paraffin oil, were not yet reported. The second objective of this original study was the comparison between two PBut-*block*-P2VP copolymer samples, of similar molecular weight but different compositions, in order to gain a deeper insight of the emulsification and stabilization process of PEG 400/paraffin oil emulsions. By this approach, a correlation will be established between the copolymer molecular characteristics and the static stability as well as the rheological properties of the emulsions.

MATERIALS AND METHODS

Materials

The PBut-*block*-P2VP copolymers were synthesized by living anionic polymerization in THF according to the technique developed by Fontanille and Sigwalt[23] and generously provided by Dr. J.P. Lerch. Two block copolymer samples, designated as copolymer **A** and **B**, were used in this study. The copolymer **A** has the following characteristics: M_n (P2VP) = 5300 g/mol; M_n (PBut) = 6900 g/mol, thus a PBut weight fraction of 0.56, and an M_w/M_n of 1.06 while those of copolymer **B** are: M_n (P2VP) = 3900 g/mol; M_n (PBut) = 10,200 g/mol, with a PBut weight fraction of 0.72, and an M_w/M_n of 1.09. The configuration of the PBut sequence corresponds to 90 mol % 1, 2 and 10 mol % trans.

Paraffin oil was purchased from Fluka and it is characterized by a specific mass of 0.86 g/cm³ and a viscosity of 138 mPa.s at 20°C whereas at 30°C the viscosity is equal to 77 mPa.s. PEG 400, purchased also from Fluka, has a specific mass of 1.13 g/cm³ and a viscosity of 120 mPa.s at 20°C.

Micellization of Block Copolymers in Paraffin Oil

For the preparation of micellar solutions, the PBut-*block*-P2VP copolymers were dissolved at 70°C in paraffin oil, close to the T_g of P2VP, at concentrations of 0.83 and 3.33 wt %, respectively, followed by a slowly cooling to room temperature. At this temperature it is interesting to notice that the micellar solution of the copolymer **A** were opalescent for all the copolymer concentrations whereas transparent solutions were obtained for copolymer **B**.

Emulsion Preparation

PEG 400/paraffin oil non-aqueous emulsions were prepared at copolymer concentrations with respect to the total emulsion

volume of 0.5, 1, and 2 wt %, respectively, and two emulsion compositions, such as 20/80 and 40/60 vol/vol. The total volume of an emulsion is fixed at 100 mL. The PBut-*block*-P2VP copolymers, used as polymeric stabilizers, were dissolved at 70°C in paraffin oil at the desired concentrations. After complete dissolution, the PEG 400, also kept at 70°C, was dispersed in the continuous paraffin oil phase with an addition rate of 2 mL/min under agitation at 20,000 rpm provided by an Ultra-Turrax T18 (IKA, Germany) homogenizer. This emulsion was further homogenized, at the same speed, for 10 min. At this stage, the emulsion temperature was around 60°C and then, the temperature was slowly decreased to room temperature.

The emulsions **E** are identified such as EA_b^a and EB_b^a, with **A** and **B** being the copolymer sample, a its concentration (wt % with respect to the total emulsion volume) and b its volume fraction of the dispersed phase.

Dynamic Light Scattering

Dynamic light scattering measurements, carried out with a Malvern Nano-ZS Zetasizer equipped with a 4 mW He–Ne laser operating at a wavelength of 532 nm, were made at a scattering angle $\theta = 173°$. Using the Stokes–Einstein equation, with the viscosity of the continuous phase, the software package of the instrument calculates the hydrodynamic diameter (volume average) D_v, the Z-average diameter, which is an intensity weighted average size and the polydispersity index PDI of the sample.

Stability and Droplet Size Characterization

The emulsion stability was investigated by using an optical analyzer TurbiScan MA2000 (Formulaction, France). The TurbiScan includes a pulsed near-infrared light source ($\lambda = 850$ nm) and a synchronous transmission (T) and a back scattering (BS) detector. In this study, the detection head scanned the entire height of the sample (about 50 mm), acquiring T and BS data each 40 μm and each 15 min over 24 h at 30°C ± 1. The average particle size of the emulsion droplets could further be estimated from the sedimentation rate.

Rheological Characterization

The rheological properties of emulsions were analyzed using a rheometer AR 2000Ex-TA instrument with a cone and plate geometry sensor (40 mm diameter, 2° cone angle). The measurements were carried out at 20°C with a gap distance of 0.05 mm. For the determination of viscoelastic properties, a frequency sweep test was performed at 20°C with an applied torque of 10 microN.m and an excitation frequency in the range of 0.01–10 Hz. Prior to all measurements, the samples were
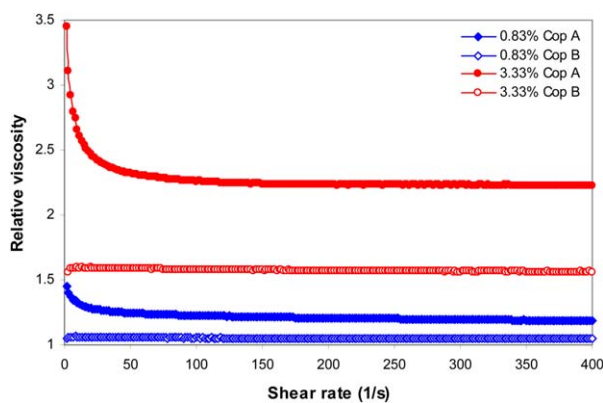
Figure 1. Relative viscosity of the micellar systems versus shear rate at 20°C for copolymer **A** and **B**, respectively, as a function of concentration. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2. ΔT profiles obtained after 24 h at the top of the cell for 20/80 PEG 400/paraffin oil emulsions as a function of the copolymer **A** and **B** concentrations. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

submitted to a shear rate of 50 s^{-1} for 30 s and equilibrated for 2 min at 20°C to standardize their history.

RESULTS AND DISCUSSION

Micellization Behavior

The colloidal characteristics of the PBut-*block*-P2VP block copolymers, used in this study as stabilizers for the PEG 400/paraffin oil emulsions, are of interest in order to gain an insight in the mechanism involved in the emulsion stabilization. The driving force for the micellization of these copolymers, with almost identical molecular weight but different compositions, is the solvent selectivity for different blocks. In view of the solubility parameters, these copolymers form micelles with a P2VP core and PBut corona in paraffin oil. In fact, the solubility parameters for paraffin oil and PBut are in the range of 16–17.0 MPa$^{1/2}$ whereas for P2VP sequences and PEG 400 are around 21 MPa$^{1/2}$.[13]

The micellization of copolymer **A** and **B** in paraffin oil was investigated as a function of the concentration and temperature. The colloidal characteristics at 20°C and 30°C, such as Z-average, D_v, and PDI, are given in Table I.

This table shows a weak dependence between the micellar particle sizes and the concentration for both copolymer samples. Furthermore, it was noticed that copolymer **A**, with weight composition close to 50/50 wt %, is characterized by higher colloidal sizes and higher PDI values than copolymer **B**. To some extent, this difference might be attributed to the partial aggregation of the copolymer **A** micelles having shorter PBut sequences than copolymer **B**. A temperature increase from 20 to 30°C, leads to a slight increase of the micellar sizes for both copolymer samples, as outlined in Table I.

For these micellar solutions it was of interest to analyze their viscosity as a function of the shear rate. The variation of the relative viscosity as a function of the shear rate, at 20°C, for both copolymer samples is given in Figure 1.

As expected, the relative viscosity increases with increasing the copolymer concentration from 0.83 to 3.33 wt % for both
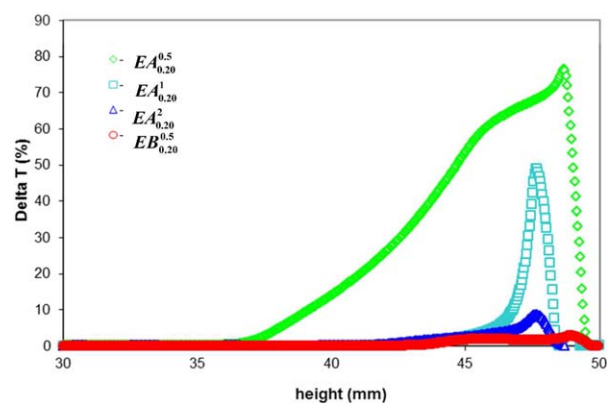
copolymer samples. Moreover, it appears that copolymer **B** is characterized by a Newtonian flow behavior whereas for copolymer **A** an important shear thinning effect was noticed for shear rates below 100 s^{-1}. This viscosity decrease under shear might be due to the disruption of the interactions between colloidal particles, which are more important for the copolymer **A** with a thinner PBut corona layer than for copolymer **B**. As shown in Figure 1, this effect is enhanced by increasing the copolymer **A** concentration. A similar behavior is also observed for these micellar solutions at 30°C, as shown in Figure S1 (Supporting Information).

Emulsion Stability and Droplet Size

Non-aqueous emulsions, with compositions of 20/80 and 40/60 PEG 400/paraffin oil, were obtained by high speed emulsification at 70°C at a copolymer **A** and **B** concentrations of 0.5, 1 and 2 wt/wt %, respectively. Under these conditions, it might be admitted that both copolymer samples become molecularly dispersed in the presence of PEG 400 and paraffin oil phases. These emulsions were characterized by their static stability, droplet size, and rheological behavior in order to establish a correlation between the emulsions properties and the copolymer molecular characteristics.
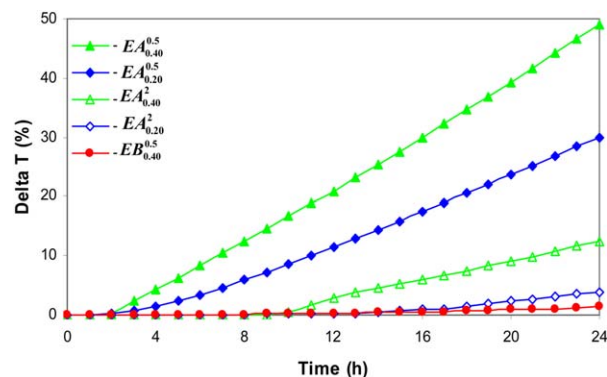

Figure 3. Evolution of ΔT at the top of the cells as a function of time for **EA** and **EB** emulsions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Sedimentation Rates and Droplet Size for **EA** and **EB** Emulsions Obtained Over 24 h at the Top of the Cell

Emulsions	Sedimentation rate (μm/min)	Droplet size (μm)
$EA_{0.40}^{0.5}$	3.81	23.0
$EA_{0.40}^{1}$	1.05	11.3
$EA_{0.40}^{2}$	0.54	8.7
$EB_{0.40}^{0.5}$	0.50	7.5
$EB_{0.40}^{1}$	$\sim$0	n.d
$EB_{0.40}^{2}$	$\sim$0	n.d
$EA_{0.20}^{0.5}$	3.50	9.0
$EA_{0.20}^{1}$	0.45	3.0
$EA_{0.20}^{2}$	0.30	2.6
$EB_{0.20}^{0.5}$	0.43	3.1
$EB_{0.20}^{1}$	$\sim$0	n.d
$EB_{0.20}^{2}$	$\sim$0	n.d

n.d = Not determined within the time range of 24 h.

The static emulsion stability was evaluated by the Turbiscan optical transmission every 15 min over 24 h. The transmission profiles at 0 h were taken as baselines and, therefore, subtracted from the profiles corresponding to different times in order to visualize more precisely the variations between each measurement. A local variation of the droplets concentration, indicating migration phenomena, was noticed especially for **EA** emulsions at the top of the cells. This migration phenomenon, displayed by local variations of the transmission intensity, is due to sedimentation of the PEG 400 droplets having a higher specific mass of 1.13 g/cm^3. It is interesting to note that the transmission is equal to 0 in the middle of the cell, indicating no droplet size variation and, therefore, the absence of coalescence.

Delta T (ΔT) profiles obtained at the top of the cells after 24 h are given in Figure 2 for $EA_{0.20}$ and $EB_{0.20}$ emulsions as a function of the copolymer concentration.

The transmission profiles, illustrated in Figure 2, indicate that higher ΔT values correspond to lower stability. In fact, the emulsions stability decreases with decreasing copolymer **A** concentration from 2 to 0.5 wt %. The emulsions prepared in the presence of 1 and 2 wt % of copolymer **B** were completely stable within 24 h whereas at a copolymer **B** concentration of 0.5 wt % only a slight instability could be noticed. At this point, it should be kept in mind that an almost instantaneous phase separation occurs in the absence of block copolymers.

From the transmission profiles, recorded every 15 min over 24 h, it became possible to follow the evolution of the ΔT as a function of time for each emulsion sample. This evolution is illustrated in Figure 3 for two copolymer concentrations of 0.5 and 2 wt %, respectively.

From this figure it clearly appears, as expected, that the most stable **EA** emulsions are obtained with a copolymer concentration of 2 wt/wt %. Moreover, at a given copolymer **A** concentration, it turns out that the emulsion stability is also influenced by the volume fraction of the PEG 400 dispersed phase and, therefore, higher stability being obtained for 20/80 PEG 400/paraffin oil emulsions. A slight variation of the ΔT within 24 h was only observed for $EB_{0.40}^{0.5}$ with a low copolymer concentration and high volume fraction of the dispersed phase. This is a confirmation that copolymer **B**, with a higher PBut content, is a more efficient stabilizer than copolymer **A**.

From the transmission profiles recorded every 15 min over 24 h it was possible to estimate the sedimentation velocities and consequently the droplet size and the corresponding values are given in Table II.

From this table it appears that all emulsion samples are micron sized. As expected, by increasing the copolymer concentration, a decrease of the droplets size is observed. This situation is clearly shown for **EA** emulsions. For **EB** emulsions, the droplet size could only be estimated, within the time range of 24 h, for emulsions stabilized by the lowest copolymer **B** concentration such as 0.5 wt %. Moreover, for higher copolymer **B** concentrations, no sedimentation was observed in this time range of 24 h and thus it was not possible to determine the corresponding
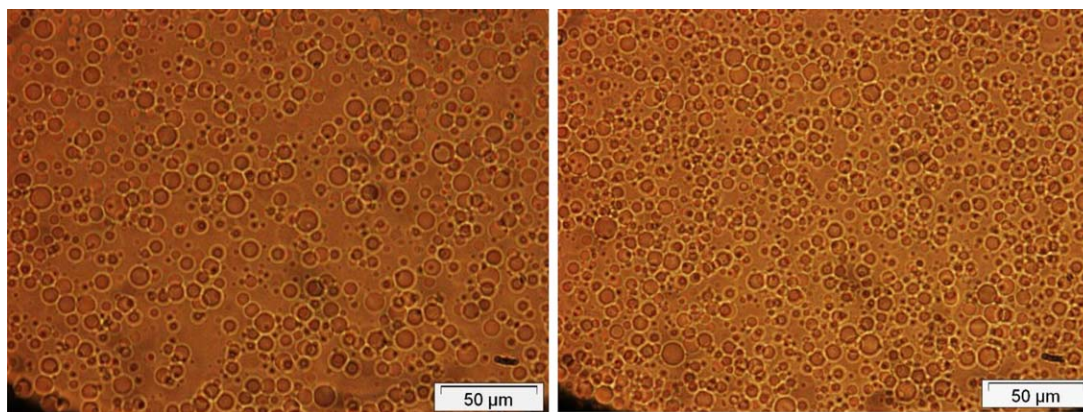

Figure 4. Photomicrographs of $EA_{0.20}^{1}$ and $EB_{0.20}^{1}$ emulsions obtained with an Olympus BX51 microscope. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
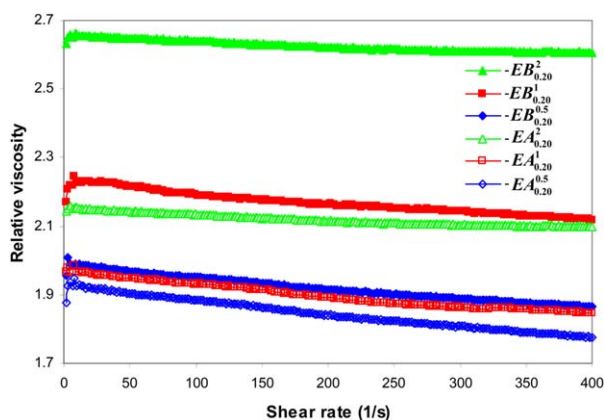
Figure 5. Relative viscosity versus shear rate at 20°C for 20/80 PEG 400/paraffin oil emulsions stabilized with a copolymer **A** and **B** concentration of 0.5, 1, and 2 wt %, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

droplet size. However, it can reasonably be admitted that the droplet size is definitely smaller for **EB** emulsions than for **EA** ones at copolymer concentrations of 1 and 2 wt % and fixed volume fraction. This conclusion is confirmed by photomicrographs of $EA_{0.20}^1$ and $EB_{0.20}^1$ emulsions which are given in Figure 4.

From this comparison, it clearly appears that the droplet size and the polydispersity are smaller for $EB_{0.20}^1$ than those obtained for $EA_{0.20}^1$ emulsion.

Rheological Behavior

The emulsion rheological properties, such as viscosity as a function of the shear rate and of time, are of interest for practical applications due to the fact that they provide important information about the emulsion flow behavior and shear stability. In practice, as outlined by Sherman,[24] these characteristics are influenced by the volume fraction of the dispersed phase, the viscosity ratio of the phases in presence, the droplet size and polydispersity as well as the viscoelastic properties of the emulsifier film absorbed at the interface.

Figure 5 shows the variation of the relative viscosity η/η_0, η_0 being the paraffin oil viscosity, as a function of the shear rate for 20/80 PEG 400/paraffin oil emulsions as a function of the copolymer **A** and **B** concentration at 20°C.

From this figure an important shear thinning effect can be noticed for all the samples with the exception of the $EA_{0.20}^2$ and $EB_{0.20}^2$ emulsions, characterized by a PEG 400 dispersed phase volume fraction of 0.20 and stabilized with a copolymer concentration of 2 wt/wt %. On the contrary, this shear thinning effect is even more pronounced for emulsions having a dispersed phase volume fraction of 0.40 as shown in Figure S2 (Supporting Information). For emulsions with a high dispersed phase volume fraction, this shear thinning effect is mainly due, on one hand, to the deformation of the droplets as suggested by Saiki et al.[25] and on the other to the disruption of inter-droplet interactions as outlined by Yaron et al.[26] This disruption might even be enhanced at the high shear rate and, therefore, the ratio η_{400}/η_{100} is representative of the flow characteristics

under shear. These values, as well as the relative viscosity values, are summarized in Table III for all the emulsion samples.

From this table it can be seen that as well the **EA** as the **EB** emulsions, with a dispersed phase volume fraction of 0.40, are characterized by a lesser shear stability than those obtained with a PEG 400 volume fraction of 0.20. Moreover, for all the emulsion samples, an increase of the shear stability was observed with increasing copolymer concentration. At a given copolymer concentration and dispersed phase volume fraction copolymer **B** provides a slightly higher shear stability than copolymer **A**. This behavior might be a consequence of the droplet size difference between **EA** and **EB** emulsions.

As a general trend for the η_{rel} values at a shear rate of 100 s^{-1}, it was noticed that, at a fixed volume fraction φ, the relative viscosity increases with the copolymer concentration as a consequence of the droplet size reduction. At a fixed copolymer concentration, the η_{rel} values increases also, as expected, with the dispersed volume fraction. By comparing **EA** with **EB** emulsions, at a given copolymer concentration and φ, it can be pointed out that the higher relative viscosity values are systematically obtained for **EB** emulsions. For instance, by comparing the $EB_{0.20}^{0.5}$ with the $EA_{0.20}^1$ and the $EB_{0.20}^1$ with the $EA_{0.20}^2$ emulsions it turns out that identical η_{rel} values are obtained by using a two times smaller copolymer **B** concentration.

Furthermore, it is of common practice for emulsion characterization to determine the viscosity as a function of time under constant shear rate, as suggested by Rodríguez-Valverde et al.[27] This stability is determined at a shear rate of 100 s^{-1}, which is similar to the shearing involved in emulsions handling. This evolution, illustrated in Figure S3 (Supporting Information) for 20/80 PEG 400/paraffin oil emulsions, clearly demonstrates that these emulsions are stable under this shear rate.

The rheological behavior was completed by the determination of the emulsion viscoelastic characteristics and in particular of the loss modulus G'', which is characteristic for the viscous properties. The evolution of the G'' as a function of the

Table III. η_{400}/η_{100} Ratio and Relative Viscosities η_{rel} at a Shear Rate of 100 s^{-1} for PEG 400/Paraffin Oil Emulsions at 20°C

Emulsions	Volume fraction φ	$\eta400/\eta100$	ηrel
$EA_{0.40}^{0.5}$	0.40	0.70	3.35
$EA_{0.40}^1$		0.76	4.05
$EA_{0.40}^2$		0.80	4.67
$EB_{0.40}^{0.5}$		0.72	4.93
$EB_{0.40}^1$		0.78	5.37
$EB_{0.40}^2$		0.81	6.64
$EA_{0.20}^{0.5}$	0.20	0.93	1.89
$EA_{0.20}^1$		0.95	1.93
$EA_{0.20}^2$		0.98	2.14
$EB_{0.20}^{0.5}$		0.95	1.95
$EB_{0.20}^1$		0.97	2.19
$EB_{0.20}^2$		0.99	2.64

Table IV. G'' Values as a Function of the Frequency for All the Emulsion Samples at 20°C

| Emulsions | G' (Pa) | | | G'' (Pa) | | |
| | Frequency (Hz) | | | | | |
	0.1	1	10	0.1	1	10
$EA^{0.5}_{0.40}$	2.17×10^{-3}	0.05	2.38	0.32	3.37	32.29
$EA^{1}_{0.40}$	2.25×10^{-3}	0.07	2.64	0.35	3.76	37.98
$EA^{2}_{0.40}$	2.65×10^{-3}	0.08	3.10	0.40	4.26	43.38
$EB^{0.5}_{0.40}$	5.35×10^{-3}	0.06	3.16	0.35	3.98	39.92
$EB^{1}_{0.40}$	5.85×10^{-3}	0.07	3.71	0.41	4.36	43.54
$EB^{2}_{0.40}$	9.45×10^{-3}	0.16	4.48	0.50	5.13	50.91
$EA^{0.5}_{0.20}$	8.09×10^{-5}	6.49×10^{-3}	0.06	0.14	1.45	14.57
$EA^{1}_{0.20}$	2.28×10^{-4}	0.01	0.13	0.15	1.54	15.48
$EA^{2}_{0.20}$	3.71×10^{-4}	0.02	0.24	0.18	1.80	18.18
$EB^{0.5}_{0.20}$	1.96×10^{-4}	0.02	0.16	0.17	1.69	16.96
$EB^{1}_{0.20}$	3.91×10^{-4}	0.02	0.18	0.19	1.88	18.98
$EB^{2}_{0.40}$	6.49×10^{-4}	0.03	0.28	0.22	2.23	20.81

frequency is given in Table IV for all the emulsion samples. The values of the storage modulus G', which represent the energy stored in the system during oscillation due to the elastic deformation of the droplets, are negligible with respect to G''. These values are provided in Table IV.

From this table it can be observed that G'' values increase linearly with the frequency for all the copolymer concentrations and emulsion compositions. At a given volume fraction φ and for all the frequencies the G'' values increase with increasing the copolymer concentration. For a fixed copolymer concentration and φ, it turns out that the G'' values are systematically higher for **EB** emulsions than for those obtained with copolymer **A**. A direct correlation exists between G'' and relative viscosities values for all the emulsion samples. According to Niraula et al.,[28] these emulsions, where G'' response was dominant over G', spread easily when they are applied to human skin.

CONCLUSIONS

The concept of non-aqueous emulsions was extended in the present study in order to have a better understanding of the emulsifying and stabilizing mechanism of well-defined block copolymers. PEG 400/paraffin oil biocompatible emulsions were developed in the presence of two PBut-*block*-P2VP block copolymers, with similar molecular weights but different compositions, and a comparison between the emulsions characteristics was performed. The guideline for selecting a block copolymer as stabilizer for non-aqueous emulsions was based on the solubility parameter concept. Indeed, these block copolymers form micelles in paraffin oil having a P2VP core and a PBut corona. The emulsion characteristics, such as static stability, droplet size and rheological behavior, determined as a function of the copolymer concentration for two dispersed phase volume fractions, were correlated with the copolymer molecular characteristics. It was shown that all the emulsions are micron-sized and that those stabilized by copolymer **B**, having a longer paraffin oil soluble PBut sequence, are characterized by smaller droplet sizes than **EA** emulsions. Consequently, **EB** emulsions are significantly more stable within 24 h than **EA** ones. Concerning the rheological characteristics it appeared that, at a given copolymer concentration and dispersed phase volume fraction, higher values of η_{rel} and G'' are obtained for emulsions prepared in the presence of copolymer **B** than for those stabilized by copolymer **A**.

Finally, it was demonstrated that copolymer **B,** with a longer paraffin oil soluble PBut sequence, corresponding to a weight fraction of around 0.72, is a more efficient emulsifier and stabilizer than copolymer **A** having a PBut weight fraction of 0.56.

From a practical point of view, this investigation may be of interest not only for a fundamental aspect but also for the drug-loaded non-aqueous and lubricant formulations.

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