Polymerization in Organized Systems

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1 Introduction

The effect of monomer organization on polymerization and polymer properties is illustrated by a critical survey of some typical polymerization experiments conducted in certain organized systems. For comparison, in most of the cases, the same polymerizations are performed under isotropic conditions. Monomer organization may prove, at least in principle, of critical importance in polymerization and it can be achieved in various ways including the use of thermotropic liquid crystalline media,[1,2] orientation at liquid–liquid interfaces,[3] and organization in micellar[4–6] or vesicular media.[7] It should be noted that these organized media are interrelated and recent findings established the fact that common molecular structural features lead to the formation of organized systems either in the bulk or in the dispersed phase. On the other hand, in discussing organized polymerization, we proceed from thermotropic liquid crystalline media to polymerization at liquid–liquid interfaces and then to micellar and vesicular phases to coincide with the historical development of the subject, and perhaps with the increasing complexity of the respective media.

The significance of polymerization in organized media is primarily attributable to its resemblance to biological reactions, which usually occur in organized systems.[7] Furthermore, monomer organization may affect polymerization kinetics, polymer structure, and specifically microstructure, a polymer property that is directly related to the organization of the reacting monomers. Among the polymers of scientific and technological value prepared by polymerization in organized media, are liquid-crystal polymers[8] and polymeric surfactants,[7] which, depending on their molecular structure, may form intra- and/or inter-molecular micelles[9] or polymerized vesicles.[7] The latter aggregates retain the vesicular structure of their monomeric counterparts and since they exhibit sufficient stability

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[1] E. M. Barral II and J. F. Johnson, *J. Macromol. Sci., Rev. Macrom. Chem.*, 1979, **17**, 137.

[2] H. Kelker and R. Hatz, Handbook of Liquid Crystals, Verlag Chemie, Weinheim, 1980.

[3] Interfacial Synthesis, ed. F. Millich and C. E. Carracher, jun., Volumes I and II, Marcel Dekker, Inc., New York and Basel, 1977.

[4] C. A. Bunton, in 'Techniques of Chemistry', Vol. X Part II, ed. J. B. Jones, C. J. Sih, and D. Perlman, J. Wiley and Sons, 1976, 731.

[5] J. M. Brown in 'Colloid Science', A Specialist Periodical Report, Vol. 3, The Chemical Society, London, 1977, p. 253.

[6] E. J. R. Sudhölter, G. B. van de Langkruis, and J. B. F. N. Engberts, *Recueil*, 1980, **99**, 73.

[7] J. H. Fendler 'Membrane Mimetic Chemistry', John Wiley and Sons, New York, 1982.

[8] Liquid Crystal Polymers in 'Advances in Polymer Science', Vol. 59, 60/61 ed. M. Gordon, Springer-Verlag, Berlin New York, 1984.

[9] C. M. Paleos, C. I. Stassinopoulou, and A. Malliaris, *J. Phys. Chem.*, 1983, **87**, 251.

they are considered as the closest analogues of biological membranes. Therefore, a long-term objective, *i.e.* the formation of stabilized cell-models, has almost been accomplished.[10] These models may be used in studying membrane properties[7] and membrane transport phenomena,[11,12] in medicine as drug carriers,[13–15] and in artificial photosynthesis.[16–19]

2 Polymerization in Thermotropic Liquid Crystalline Media

The first examples[20] of reactions conducted in nematic liquid-crystalline phases were the thermal decompositions of picric acid, pyrogallol, and trinitroresorcinol. According to these early experiments, performed by Swedberg[20] in 1916, organization exerted an inhibitory effect on the rate of their thermal decomposition. In 1967, fifty-one years later, Amerik and Krentsel[21] undertook comparative investigations of the radiation-induced polymerization of vinyl oleate (a liquid crystalline monomer) in the solid, mesomorphic, and isotropic phases. They found that the morphology of the polymer depended significantly on the phase in which polymerization had occurred. Crystalline polymer was obtained when the monomer was polymerized in the solid or mesomorphic phases, and the amorphous form resulted when polymerization was conducted isotropically. Amerik *et al.*[22] also studied the polymerization of *p*-methacryloxybenzoic acid in a liquid crystalline solvent, *p*-cetyloxybenzoic acid, and they compared it with the polymerization of the same monomer in dimethylformamide. A polymer of higher molecular weight was obtained in liquid crystalline polymerization as compared to the one obtained under isotropic conditions.

Following these first liquid crystalline polymerization experiments a series of

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[10] H. F. Mark, *Agnew. Chem., Int. Ed. Engl.*, 1981, **20**, 303.

[11] J. H. Fendler, *Acc. Chem. Res.*, 1980, **13**, 7.

[12] R. Mcneil and J. K. Thomas, *J. Colloid Interface Sci.*, 1980, **73**, 522.

[13] Liposomes in Biological Systems, ed. G. Gregoriadis and A. C. Allison, Wiley-Interscience, Chichester—New York, (1980).

[14] B. E. Ryman and D. A. Tyrrell, in 'Essays in Biochemistry', Vol. 16, ed. P. N. Campbell and R. D. Marshall, Academic, New York, 1981, p. 49.

[15] L. Gros, H. Ringsdorf, and H. Schupp, *Agnew. Chem., Int. Ed. Engl.*, 1981, **20**, 305.

[16] M. Gratzel, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 981.

[17] K. Kurihara, P. Tundo, and J. H. Fendler, *J. Phys. Chem.*, 1983, **87**, 3777.

[18] K. I. Zamaraev and V. N. Parmon, *Russ. Chem. Rev.*, 1983, **52**, 1433.

[19] M. Kaneko and A. Yamada, in 'Advances in Polymer Science', Vol. 55, Springer-Verlag, Berlin—New York, 1984, p. 2.

[20] T. Swedberg, *Kolloid. Z.*, 1916, **18**, 54, 101.

[21] Y. B. Amerik and B. A. Krentsel, *J. Polym. Sci., Part C*, 1967, **16**, 1383.

[22] Y. B. Amerik, I. I. Konstantinov, and B. A. Krentsel, *J. Polym. Sci., Part C*, 1968, **23**, 231.

[23] V. E. Perplies, H. Ringsdorf, and J. H. Wendorff, *Ber. Bunsenges. Phys. Chem.*, 1974, **78**, 921.

[24] C. M. Paleos and S. Voliotis, *Isr. J. Chem.*, 1979, **18**, 192.

[25] C. M. Paleos and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, 1970, **11**, 385.

[26] E. C. Hsu and A. Blumstein, *J. Polym. Sci., Lett. Ed.*, 1977, **15**, 129.

[27] P. L. Magagnini, *Makromol. Chem. Suppl.*, 1981, **4**, 223.

[28] B. Bressi, V. Frosini, D. Lupinacci, and P. L. Magagnini, *Makromol. Chem., Rapid Commun.*, 1980, **1**, 183.

[29] U. P. Shibaev, V. M. Moissenko, Ya. S. Freidon, and N. A. Platê, *Eur. Polym. J.*, 1980, **16**, 272.

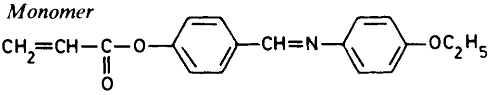
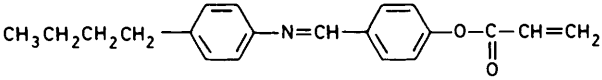
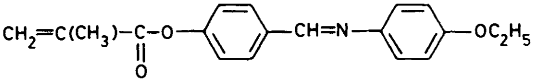
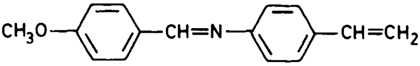
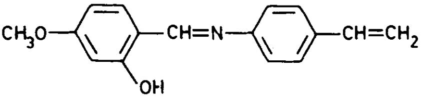
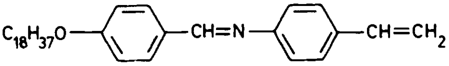
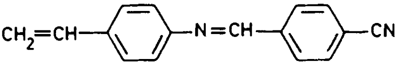
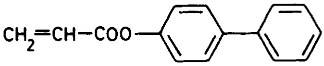
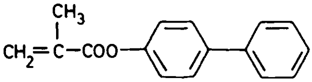
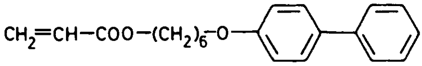
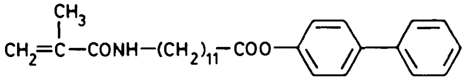
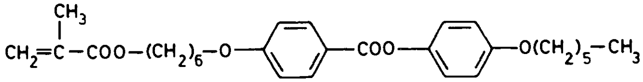
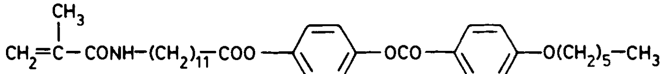
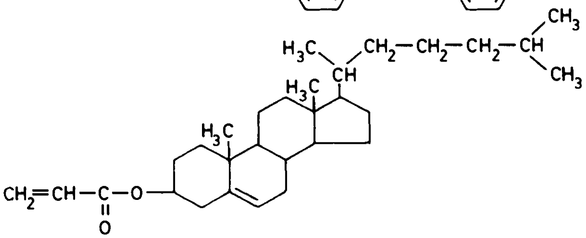
[30] H. Finkelmann, H. Ringsdorf, and J. H. Wendorff, *Makromol. Chem.*, 1978, **179**, 273.

[31] H. Finkelmann, M. Happ, M. Portugal, and H. Ringsdorf, *Makromol. Chem.*, 1978, **179**, 2541

[32] V. P. Shibaev and N. A. Platê, *Makromol. Chem.*, 1980, **181**, 1393.

[33] W. J. Toth and A. V. Tobolsky, *J. Polym. Sci., Lett., Ed.*, 1970, **8**, 289.

Table 1 *Some nematic, smectic, and cholosteric liquid crystalline monomers*

Monomer	*Ref.*
	23
	24
	23
	25
	25
	25
	26
	27
	27
	28
	29
	30, 31
	30, 32
	33

liquid crystalline monomers were prepared, the synthesis of which was based on the functionalization of appropriate mesogenic moieties with polymerizable groups. The monomers that were obtained exhibited nematic, smectic, and cholesteric phases and some of the typical liquid crystalline monomers are shown in Table 1.

A major concern during early polymerization experiments in thermotropic liquid crystalline media was the retention of mesomorphic order during polymerization in order to take complete advantage of the organization of the liquid crystalline phase. The preservation of liquid crystalline order during polymerization might be achieved by low monomer-to-polymer conversion and also by using suitable liquid crystalline mixtures in which the monomer acts as a low concentration solute in a liquid crystalline solvent. However, despite such attempts to preserve liquid crystalline order during polymerization a definite trend as far as the effect of liquid crystallinity on polymerization and polymer products is not observed. On the contrary, a critical survey of the literature on this subject reveals that there is little agreement concerning the effect of liquid crystalline order on polymerization or polymer structure. Thus, in some liquid crystalline polymerizations there is a rate acceleration, in some others retardation, while in certain other cases the polymerization rate remains unaffected. Analogously, polymerization of mesomorphic monomers leads either to the formation of liquid crystalline polymers or to regular polymers. As far as the character of the polymers is concerned (*i.e.* whether they are mesomorphic or not), it seems that the role of organization is not of crucial importance. The initial thought, that the controversy over the nature of the polymers originates from a possible destruction of the mesophase, did not prove to be an adequate explanation since it has been discovered that polymerization from isotropic melts[33a] affords liquid crystalline polymers. In addition, in a specifically designed experiment[24] in which the liquid crystalline order was preserved during polymerization by using a liquid crystalline mixture in which solvent (1) and solute (2) had similar structures, the polymer prepared was of similar structure to the one obtained isotropically, as judged by *X*-ray analysis. Recently, however, Ringsdorf and his co-workers[34] as well as Shibaev *et al.*[35,36] have determined the structural criteria required for the formation of liquid crystalline polymers. The first group of workers set forth a model which clearly describes the structural features a polymer should have in order to show liquid crystalline character. According to this model the crucial factor for the exhibition of liquid crystallinity is the existence of mesogenic groups, the motion of which must be decoupled from that of the main chain by appropriate spacer groups. However, the effect of the main chain cannot always be disregarded.[28] Depending on the position of the mesogenic group(s), two classes of liquid crystalline polymers are distinguished (Figure 1); main-chain polymers[37] (A) in

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[33a] A. Blumstein, R. B. Blumstein, S. B. Clough, and E. C. Hsu, *Macromolecules*, 1975, **8**, 73.

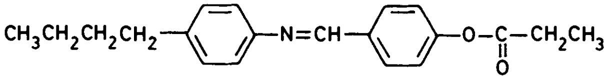
[34] J. H. Wendorff, H. Finkelmann, and H. Ringsdorf, *J. Polym. Sci., Polym. Symp.*, 1978, **63**, 73.

[35] V. P. Shibaev, N. A. Platé, and Y. A. Freidzon, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 1655.

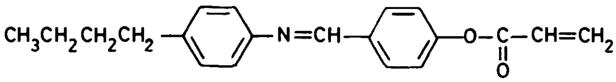
[36] V. P. Shibaev, R. V. Tal'rose, F. I. Karakhanova, and N. A. Platé, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 1671.

[37] M. G. Dobb and J. E. McIntyre in 'Advances in Polymer Science', Vol. 60/61, Springer-Verlag, Berlin New York, 1984, p. 61 and references cited therein.

which the mesogenic groups are part of the backbone, and side-chain polymers[38,39] (B) where the mesogenic group is located in the side chain. The discussion in this review is limited to side-chain liquid-crystal polymers since only this class of polymers could, in principle at least, be affected by the organizational characteristics of the mesophase. The phenomenon of liquid crystallinity in polymers, therefore, is attributed to specific structural characteristics or otherwise to an intrinsic tendency of the polymers to organize and is irrespective of the mode of polymerization by which they were prepared. Thus, the preservation of liquid crystalline order during polymerization is not a prerequisite for liquid crystalline polymer formation.



(1)



(2)

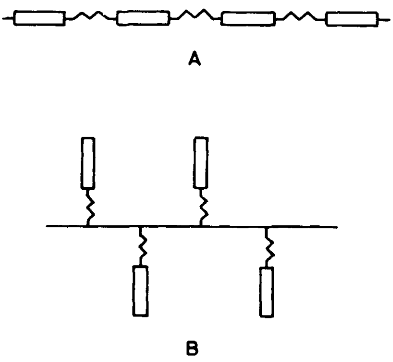


Figure 1 *The mesogenic groups of main-chain (A) and side-chain polymers (B) are decoupled from the main chain of the polymers by spacer groups of constant or variable length*

A direct consequence of these assumptions was the introduction of a novel

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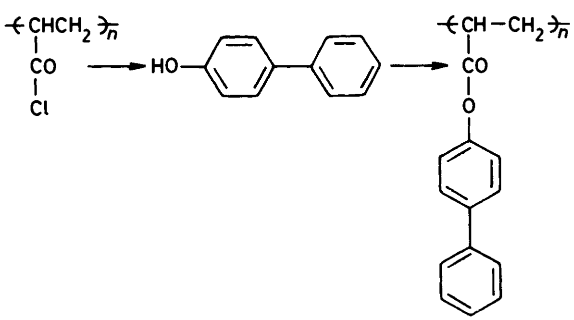
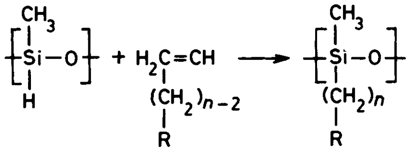
[38] H. Finkelmann and G. Rehage in *ref.* 37, p. 99 and references cited therein.
[39] V. P. Shibaev and N. A. Plate, in *ref.* 37, p. 173 and references cited therein.

method[40,41] for the synthesis under isotropic conditions of liquid crystalline polymers that involved the reaction of a reactive polymer with mesogenic moieties, for example poly(acryloylchloride) with *p*-hydroxybiphenyl according to Scheme 1. This polymer as well as similar polymers are liquid crystals since the requirement that the mesogenic groups be decoupled from the polymer backbone is fulfilled.



Scheme 1

A modified approach[42] for the synthesis of liquid crystalline polymers involves the interaction of a reactive polymer with a liquid crystalline monomer, as depicted in Scheme 2.



Where R is a mesogenic group

Scheme 2

Returning to polymerization kinetics in liquid crystalline media, a few typical examples suffice to show clearly the existing controversy. Thus, the rate was enhanced in the liquid crystalline polymerization of vinyl oleate[21] or when *p*-methacryloyloxybenzoic acid[22] was polymerized in the mesomorphic medium created by the dissolution of this monomer to *p*-cetyloxybenzoic acid, as compared to the corresponding polymerization in dimethylformamide (Figure 2). On the contrary, the rate was decreased in the polymerization of a Schiff base monomer, *e.g.* of *N*-(*p*-acryloyloxybenzylidene)-*p*-methoxyaniline,[43] as shown by the dis-

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[40] C. M. Paleos, S. E. Filippakis, and G. Margomenou-Leonidopoulou, *J. Polym. Sci., Polym. Chem. Ed.*, 1981, **19**, 1427.

[41] C. M. Paleos, G. Margomenou-Leonidopoulou, S. E. Filippakis, A. Malliaris, and Ph. Daïs, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 2267.

[42] H. Finkelmann and H. Rehage, *Makromol. Chem., Rapid Commun.*, 1980, **1**, 31.

[43] E. Perplies, H. Ringsdorf, and J. H. Wendorff, *Makromol. Chem.*, 1974, **175**, 553.

continuity observed at the mesomorphic–isotropic transition of the respective Arrhenius plot (Figure 3). In other experiments, *e.g.* the polymerization of *N*-(*p*-methoxy-*o*-hydroxybenzylidene)-*p*-aminostyrene[25] or *N*-(*p*-cyanobenzylidene)-*p*-aminostyrene,[26] the rate of the polymerization remains unaffected by the organization of the monomers. This is shown in the corresponding Arrhenius plots (Figures 4 and 5) which are practically continuous over the temperature range of mesomorphic and isotropic experiments.

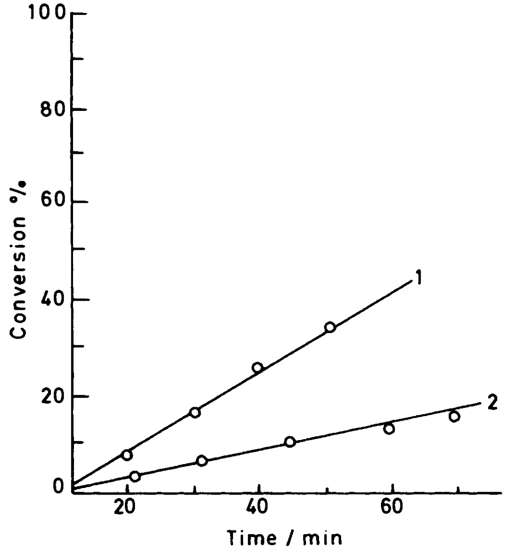

Figure 2 *Conversion–time curves of the thermal polymerization of* p-*methacryloyloxybenzoic acid in liquid crystalline medium* (*curve* 1) *and in DMF* (*curve* 2)

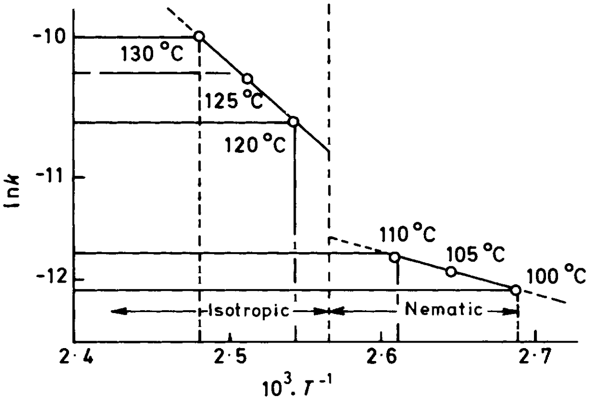

Figure 3 *Arrhenius plot of the polymerization of* N-(p-*acroyloyloxybenzylidene*)-p-*methoxyaniline in the nematic and isotropic phases*

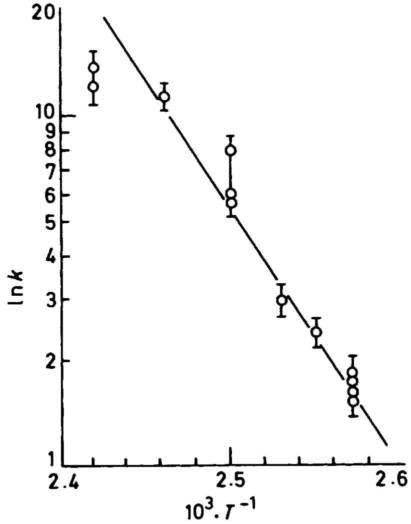

Figure 4 *Arrhenius plot of the polymerization of* N-(p-*methoxy*-o-*hydroxybenzylidene*)-p-*aminostyrene in mesomorphic and isotropic phases*

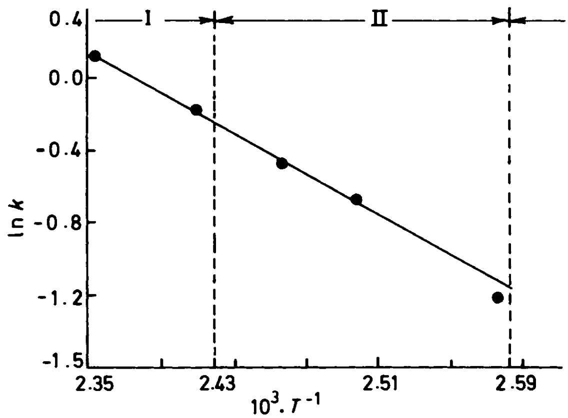

Figure 5 *Arrhenius plot of the polymerization of* N-(p-*cyanobenzylidene*)-p-*aminostyrene in liquid crystalline and isotropic phases*

From these data and other analogous results one cannot draw general conclusions about the effect of organization on polymerization in mesomorphic media. These results do, however, provide a hint for its rationalization, *i.e.* that only monomers of similar structure and polymerized under similar conditions may show the same trend in kinetic behaviour. Thus, the effect of organization on polymerization kinetics cannot easily be predicted and one should usually resort to experiment for determining the acceleration or retardation of the rate of polymerization.

3 Polymerization at Liquid–Liquid Interfaces

Interfaces are regions where two immiscible homogeneous phases come into contact. The properties of the molecules located at interfaces are differentiated from the ones dissolved in the bulk phases. Among these properties orientation[44–46] is of critical importance and its effect on polymerization will be considered below. Of the various kinds of interfaces, liquid–liquid interfaces created by two liquids of different polarity will be further discussed since this interface can be considered a model of the micro-interface created by the lipophilic core of micelles[4–7] and bulk water phase. This characterization is justified since the factors affecting micellar kinetics are strikingly similar to the ones at liquid–liquid interfaces.[46] An example of interfacial organization at a liquid–liquid interface is shown in Figure 6 where a long alkyl-chain quaternary ammonium salt, *i.e.* a surfactant molecule, is located at a water–oil interface forming an oriented monolayer. A functionalization of this compound or of any similar surfactant by a polymerizable group will result in a monomer which, in principle, can polymerize at liquid–liquid interfaces.

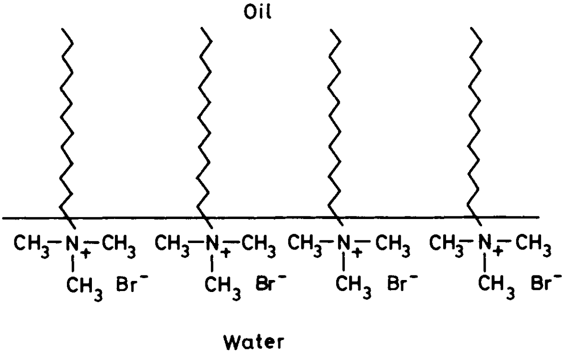

Figure 6 *Monolayer of a long alkyl-chain quaternary ammonium salt at a water–oil interface*

4-Vinyl-*N*-methylpyridinium methyl sulphate, whose polymerization was

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[44] F. M. Menger, *Chem. Soc. Rev.*, 1972, **1**, 229.

[45] F. M. Menger, *Pure Appl. Chem.*, 1979, **51**, 99.

[46] M. Spiro, in 'Essays in Chemistry', ed. J. N. Bradley, R. D. Gillard, and R. F. Hudson, Vol. 5, Academic Press, 1972, p. 65.

studied at a water–toluene interface,[47,48] was probably not the best choice from the point of view of its organizational properties at the interface, since this monomer does not bear balanced lipophilic and hydrophilic moieties. Its interfacial polymerization was, however, attempted because the mechanism of its spontaneous polymerization in isotropic media was already known[49] and therefore only the complexities originating from the interfacial mode of polymerization would have to be considered. Actually it is always good practice in novel experiments, such as interfacial polymerization, to try and limit the investigation to the interfacial parameters affecting the polymerization. In this case the quaternary nitrogen of the monomer is solvated into the aqueous phase whereas the heterocyclic ring bearing the vinyl group is located in the organic phase. Interfacial areas were increased by vigorous agitation of a water–toluene mixture leading to the formation of toluene or water droplets in the bulk phases. In fact, since the polar character of the monomer predominates over the non-polar, dispersed particles stabilized by monomer molecules as well as colloidal particles or other conglomerates are almost exclusively formed in the aqueous phase and were made visible by the scattered light in the Tyndal beam. The polymerization model, Figure 7, has been depicted as toluene droplets or cylinders in the aqueous phase stabilized by the monomers, justifying in a way the predominance of the syndiotactic[47,48] triad over the isotactic, as shown in Table 2. The small increase of the syndiotactic character of the polymer resulting from the interfacial polymerization as compared to that of isotropic polymerization, is not attributed to the inefficiency of the model (in leading to syndiotactic polymer) but rather to the fact that polymerization primarily occurs isotropically in water. This is due to the high hydrophilicity of the monomer which determines the location of the monomer and consequently its mode of polymerization. The monomer dissolves in the bulk water phase and polymerization is conducted isotropically in water. The experimental methods devised for the enhancement of interfacial modes proved almost inefficient in further controlling the stereospecificity of polymerization. It seems that only a limited number of monomers organize at the water–oil interface and polymerize according to the interfacial mode.

It should be noted that in order to avoid simultaneous micellar polymerization of the monomer in the bulk water phase, the concentration of the monomer employed in these interfacial experiments was always below its critical aggregation concentration[50] in water.

In contrast to the limited research activity on interfacial addition polymerization, significant work has been performed on polycondensation interfacial polymerization. Thus, polycondensation of diamines dissolved in water together with acid dichlorides dissolved in chlorinated solvents afforded polyamides[51,54] (Nylons) according to Scheme 3.

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[47] C. M. Paleos, *J. Polym. Sci., Polym. Lett. Ed.*, 1977, **15**, 535.

[48] C. M. Paleos, G. P. Evangelatos, Ph. Daïs, and G. Kipouros, *J. Polym. Sci., Polym. Chem. Ed.*, 1979, **17**, 1611.

[49] J. C. Salamore, B. Snider, and W. L. Fitch, *J. Polym. Sci., Polym. Chem. Ed.*, 1971, **9**, 1493.

[50] V. A. Kabanov, *Pure Appl. Chem.*, 1967, **15**, 391.

[51] P. W. Morgan, *Adv. Chem. Ser.*, 1962, **34**, 191.

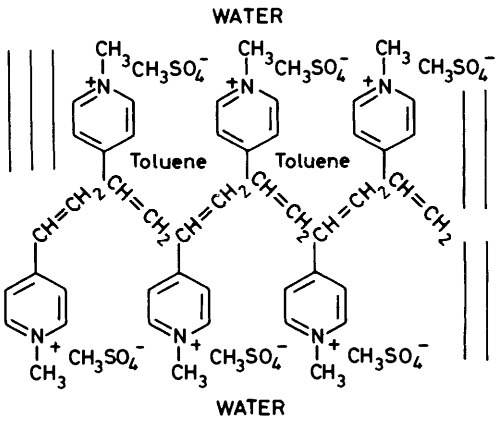
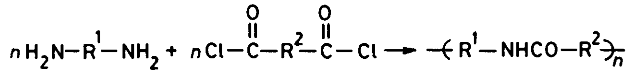


Figure 7 *Polymerization model of* 4-*vinyl*-N-*methylpyridinium methyl sulphate at a water–toluene interface* (*toluene is being solubilized by the monomer*)

Table 2 *Relative triad contents of poly*(4-*vinyl*-N-*methylpyridinium methyl sulphate*) *obtained under interfacial and isotropic conditions*

Mode of	*Isotactic*		*Heterotactic*		*Syndiotactic*		P_m*	
polymerization	*exp.*	*calc.*	*exp.*	*calc.*	*exp.*	*calc.*	*exp.*	*calc.*
Interfacial	22.13	19.68	44.50	49.46	33.33	30.85	0.465	0.555
Isotropic	25.88	27.24	52.82	50.01	21.34	22.75	0.508	0.522

* P_m is the probability of isotactic addition according to the Bernoulli mechanism of polymerization



$$n\,H_2N-R^1-NH_2 + n\,Cl-\overset{\overset{O}{\|}}{C}-R^2-\overset{\overset{O}{\|}}{C}-Cl \longrightarrow -\!\!\left(R^1-NHCO-R^2\right)\!\!-_n$$

Scheme 3

Owing to the very nature of polycondensation, properties that are directly associated with organization, such as tacticity, cannot be affected in this case. However, high concentration of the reactants at the interface leads to the formation, at low temperatures, of higher molecular weight polymers compared to the ones formed under isotropic conditions. On the other hand, bulk phases in interfacial polycondensations serve as media for the storage of the reactants and, since polymerization occurs only at the interface, the use of absolutely pure reactants is not necessary as the impurities remain in the bulk phase.

Interfacial synthesis[3] in general (and specifically polyamides,[52] polyester-

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[52] *Ref.* 3, Vol. II, p. 157.

amides,[53] polyurethanes,[54] polyureas,[55] and polyphosphonates[56]) have been extensively reviewed recently.

4 Polymerization in Micellar Systems

Micelles[4–7] are organized systems, usually formed in water by the aggregation of 30– 150 surfactant molecules when their concentration exceeds the so-called critical micelle concentration (c.m.c.). The hydrophobic effect[57] is the unique organizing force (repulsion by the solvent instead of attraction) at the site of organization that is responsible for the assembly of surfactants. The shapes taken by micelles depend on the concentration of the surfactant; at relatively low concentration the aggregates may acquire a spherical shape (Figure 8), elongating at higher concentrations and becoming rod-like (Figure 8), and at still higher concentrations becoming transformed to lyotropic liquid crystals.[58,59] It has to be noted, however, that these are oversimplified pictures of micellar structure, which is still a matter of constructive controversy.[60–62] It is certain, however, that a lipophilic core consisting of the hydrocarbon chains is formed separated by an interface (the so called Stern layer or Stern region) from the bulk aqueous phase in which head groups and (at least) some counter-ions are located. However, most of the counter-ions are found in the Gouy–Chapman electrical double-layer where they are dissociated from the micelle and are free to exchange with ions distributed in the bulk aqueous phase (Figure 9).[63] As already mentioned, the micro-interfaces that are formed in micelles resemble liquid–liquid interfaces and therefore the chemistry in micellar systems should show similarities to the chemistry at regular liquid–liquid interfaces. The interface of reversed micelles,[64,65] formed in an organic solvent, can also be considered of similar nature, having analogous properties. These systems, however, are not further discussed in this review.

A characteristic property of molecules assembling to form micelles or of compounds solubilizing into them is organization, and advantage is taken of this property in micellar polymerization. Thus, in micelle-forming molecules polymerizable groups are introduced and the c.m.c. of the monomers is determined. Polymerization is conducted comparatively under micellar conditions, *i.e.* at a concentration of the monomer in water exceeding the c.m.c., and in isotropic media in which its concentration is below the c.m.c. Some examples illustrating micellar effects on polymerization and polymer products are described below.

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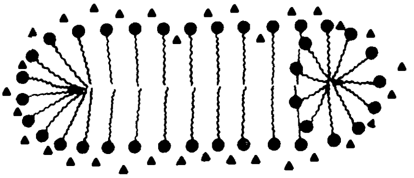
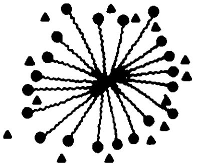
[53] *Ref.* 3, Vol. II, p. 209.
[54] *Ref.* 3, Vol. II, p. 231.
[55] *Ref.* 3, Vol. II, p. 269.
[56] *Ref.* 3, Vol. II, p. 309.
[57] C. Tanford, *Science*, 1978, **200**, 1012.
[58] P. A. Winsor, *Chem. Rev.*, 1968, **68**, 2.
[59] G. W. Gray and P. A. Winsor, in 'Advances in Chemistry Series', ed. R. F. Could, American Chemical Society, Washington D.C., 1967, p. 1.
[60] F. M. Menger, *Acc. Chem. Res.*, 1979, **12**, 11 and references cited therein.
[61] F. M. Menger and D. W. Doll, *J. Am. Chem. Soc.*, 1984, **106**, 1109.
[62] P. Fromherz, *Ber. Bunsenges. Phys. Chem.*, 1981, **85**, 891.
[63] L. R. Fisher and D. G. Oakenfull, *Chem. Soc. Rev.*, 1977, **6**, 25.
[64] H. F. Eicke and H. Christen, *Helv. Chim. Acta*, 1978, **61**, 2258.
[65] J. H. Fendler, *J. Phys. Chem.*, 1980, **84**, 1485.



Rod-like Micelle



Spherical Micelle

Figure 8 *Schematic representation of spherical and rod-like micelles:* ● *head group,* ▲ *counter ion*

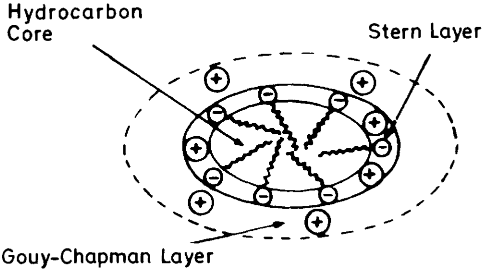


Figure 9 *A cross-section of a micelle showing the lipophilic core as well as Stern and Gouy-Chapman layers*

The spontaneous polymerization of 4-vinylpyridine protonated salts[66] in aqueous solutions takes two different routes depending upon whether the concentration of the monomer during polymerization is above or below the critical micelle concentration. Polymer I (1,6-ionene polymer) was obtained when the concentration of the monomer was below the c.m.c. and polymer II (1,2-addition polymer) when it exceeded the c.m.c., the polymerization being conducted in micellar media (Scheme 4). However, although in this case micellar organization modifies drastically the course of polymerization, the microstructure of the 1,2-

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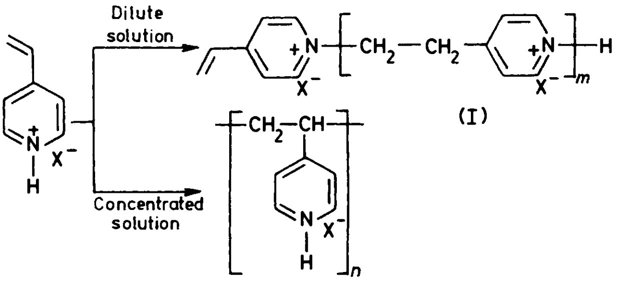
[66] I. Mielke and H. Ringsdorf, *Makromol. Chem.*, 1972, **153**, 307.

polymer as shown by ^{13}C n.m.r. studies is not affected by micellar orientation.[67] Apparently the organization imposed by the micellar aggregation is not the appropriate one to affect the tacticity of the polymer although the vinyl group is located on the rigid heterocyclic ring.



(II)

Scheme 4

Another characteristic example showing the effect of micellar structure is the polymerization of sodium 10-undecenoate (3).[68] Polymerization of this monomer was in practice accomplished only in micellar media, leading at high concentration to 'intermolecular' micelles[9] composed of 'intramolecular' polymeric micelles and establishing the fact that micellar formation is necessary for the polymerization of this salt. The effect observed is attributed to the enhancement of the rate of propagation due to the localization of monomer double bond within the micellar core. In a similar fashion the same monomer has been polymerized[69] from its lyotropic liquid crystalline media, showing again the relationship between micellar and lyotropic liquid crystalline media.

(3)

Recently a common quaternary ammonium salt, trimethyldodecylammonium bromide, has been functionalized by the introduction of the polymerizable allyl group in place of a methyl group. Polymerization[70] was achieved by γ-irradiation under both micellar and isotropic conditions. The radiolysis products of water, however, exerted a destructive effect on the polymer obtained by the isotropic polymerization. Presumably in those isotropic experiments where micelles are not formed, the long aliphatic chains are totally exposed to the products of water

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[67] C. M. Paleos and Ph. Daïs, *J. Polym. Sci., Polym. Chem. Ed.*, 1978, **16**, 1495.
[68] C. E. Larrabee and E. D. Spraque, *J. Polym. Sci., Polym Lett. Ed.*, 1979, **17**, 749.
[69] R. Thundathil, J. O. Stoffer, and S. E. Friberg, *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**, 2629.
[70] C. M. Paleos, Ph. Daïs, and A. Malliaris, *J. Polym. Sci., Polym. Chem. Ed.*, 1984, **22**, 3383.

radiolysis which are usually responsible for the formation of by-products. The main conclusion of this work is that polymerization occurs in an intramicellar fashion as judged by the fact that the mean micellar aggregation number *n* of the polymerized micelle was found equal to the aggregation number of the monomeric micelle, *i.e.* equal to 33 ± 3 corresponding to a mean molecular weight of the polymer of 11 000 ± 1 000 daltons.

It has, however, to be noticed that micellar structure does not always affect the polymerization or polymer products. Thus the radiation-induced polymerization of 3-n-dodecyl-1-vinylimidazolium iodide[71] and the polymer obtained by this micellar polymerization are not affected by micellar organization. In this case it is reasonable to adopt Menger's model[60,61] for the interpretation of the experimental data. According to this model a spherical micelle is a rather disorganized aggregate in which the Stern region, apart from the polar heads, also includes a significant fraction of the alkyl chains that are free to move about. In this region there is a considerable alkyl-chain–water contact rather than an ion double-layer shielding the non-polar nucleus. Thus, the imidazolium ring bearing the vinyl group is able to move without significant restriction in an environment that is not so much organized as predicted by older models.[60]

From the above results one cannot, therefore, draw general conclusions concerning the effects of micellar organization on polymerization and polymer products.

5 Polymerization in Vesicular Media

Liposomes[7,72] and surfactant vesicles[7,72,73] are smectic mesophases of closed phospholipid/synthetic surfactant bilayer structures. They are spherical or ellipsoidal and any that are multicompartmented can be transformed to single compartment vesicles by sonication as shown in Figure 10. The term 'vesicles' is used, for simplicity, to describe the above mentioned structures regardless of their chemical composition (see *ref.* 96).

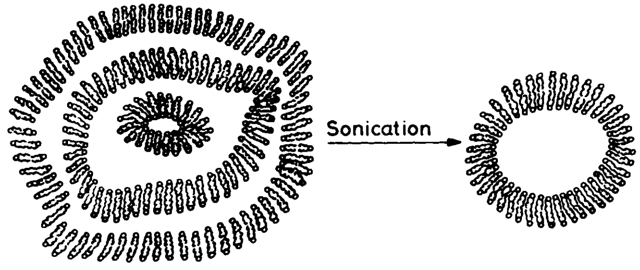

Figure 10 *Transformation of a multi-compartment vesicle to single compartment through sonication*

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[71] C. M. Paleos, S. Voliotis, G. Margomenou-Leonidopoulou, and Ph. Daïs, *J. Polym. Sci., Polym. Chem. Ed.*, 1980, **18**, 3463.

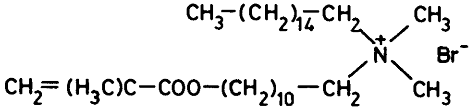
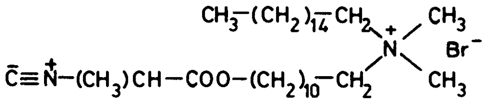
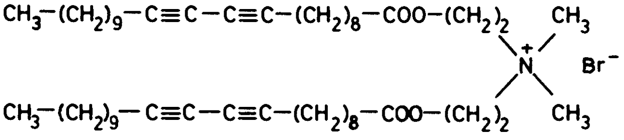
[72] J. H. Fendler, *Acc. Chem. Res.*, 1980, **13**, 7.

Vesicles are closer analogues than micelles of biological membranes and their kinetic stability,[65] as compared to the dynamic character of micelles, is responsible for their diverse applications, *e.g.* in separating charges, in artificial photosynthesis,[16–19] in drug delivery,[13–15] in reactivity control[7,74] and in the duplication of many membrane-mediated processes.[15]

The molecular structural characteristic[73,75] of vesicle-forming amphiphiles is usually the existence of two long alkyl chains, in contrast to the one required for the formation of micelles, coupled with a polar head such as a quaternary ammonium, carboxylate, sulphate, sulphonate, or phosphate group. Formation of vesicles has also been reported from single[76] and triple[77] chain amphiphiles and also from compounds[78–80] bearing a mesogenic moiety, *i.e.* the typical structure of thermotropic liquid crystals, suitably functionalized by a flexible tail or flexible tails and a polar head. Thus, according to Kunitake,[78] the liquid crystalline nature of bilayers (natural and synthetic) is the cause and not the result of bilayer formation.

In these amphiphiles polymerizable groups may be introduced in such a way that the organizational characteristics of the original vesicles are more or less preserved. Some typical vesicle-forming monomers, showing the diversity of molecular structures that exhibit this activity, are given in Table 3.

Table 3 *Some typical vesicle-forming monomers*

Monomer	*Ref.*
	82
	98
	89

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[73] T. Kunitake, *J. Macromol. Sci., Chem.*, 1979, **A13**, 587.

[74] J. F. Fendler, *Pure Appl. Chem.*, 1982, **54**. 1809.

[75] T. Kunitake and Y. Okahata, *Bull. Chem. Soc. Jpn.*, 1978, **51**, 1872.

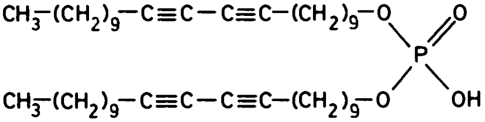
[76] W. R. Hargreaves and D. W. Deamer, *Biochemistry*, 1978, **17**, 3759.

[77] T. Kunitake, N. Kimizuka, N. Higashi, and N. Nakashima, *J. Am. Chem. Soc.*, 1978, **106**, 1978.

[78] T. Kunitake and Y. Okahata, *J. Am. Chem. Soc.*, 1980, **102**, 549.

[79] Y. Okahata and T. Kunitake, *J. Am. Chem. Soc.*, 1980, **102**, 5231.

[80] Y. Okahata and T. Kunitake, *Ber. Bunsenges. Phys. Chem.*, 1980, **84**, 550.



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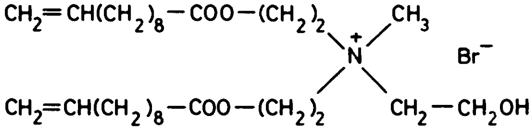

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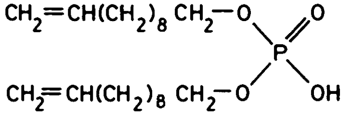

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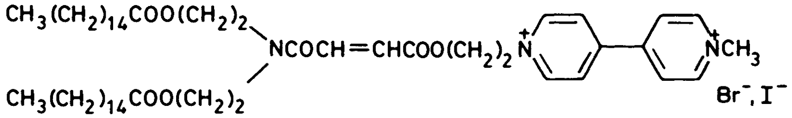
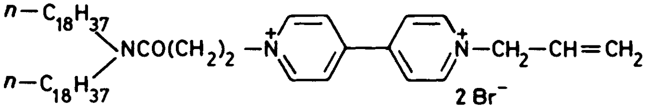
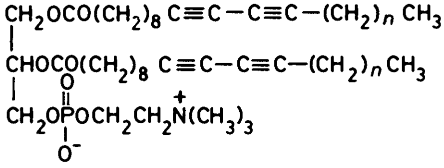


104



91



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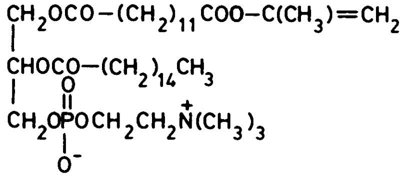

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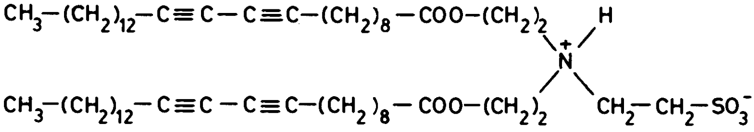

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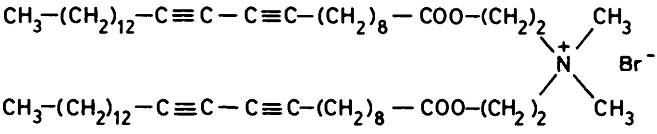
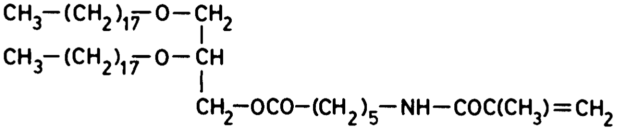


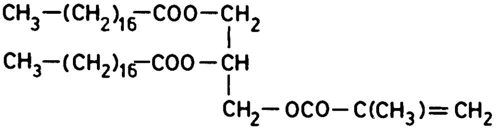
106

$HOOC-(CH_2)_8-C\equiv C-C\equiv C-(CH_2)_8-COOH$ 86



86

$$\begin{array}{l} CH_3-(CH_2)_{17}-O-CH_2 \\ CH_3-(CH_2)_{17}-O-CH \\ \qquad\qquad\quad CH_2-OCO-(CH_2)_5-NH-COC(CH_3)=CH_2 \end{array}$$



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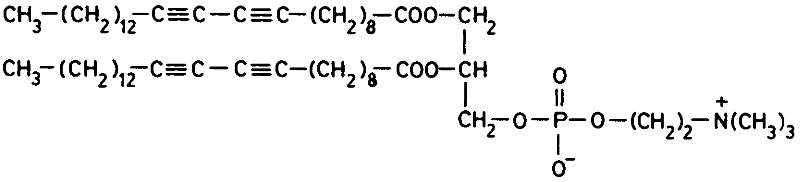
$$\begin{array}{l} CH_3-(CH_2)_{16}-COO-CH_2 \\ CH_3-(CH_2)_{16}-COO-CH \\ \qquad\qquad\quad CH_2-OCO-C(CH_3)=CH_2 \end{array}$$



107

$$\begin{array}{l} CH_3-(CH_2)_{12}-C\equiv C-C\equiv C-(CH_2)_8-COO-CH_2 \\ CH_3-(CH_2)_{12}-C\equiv C-C\equiv C-(CH_2)_8-COO-CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CH_2-O-\overset{O}{\underset{O^-}{P}}-O-(CH_2)_2-\overset{+}{N}(CH_3)_3 \end{array}$$

Investigations into the polymerization of 'monomeric' to 'polymerized' vesicles[81–101] were prompted by the need to obtain vesicles of enhanced stability and of controllable permeability and size. In order to take advantage of existing topochemical control, polymerization was conducted in the vesicular phase using conventional polymerization methods. For several vesicle-forming monomers it

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[81] D. S. Johnston, S. Sanghera, M. Pons, and D. Chapman, *Biochem. Biophys. Acta*, 1980, **602**, 57.

[82] S. L. Regen, B. Czech, and A. Singh, *J. Am. Chem. Soc.*, 1980, **102**, 6639.

[83] S. L. Regen, A. Singh, G. Oehme, and M. Singh, *J. Am. Chem. Soc.*, 1982, **104**, 791.

[84] S. L. Regen, Y. Yamaguchi, N. K. P. Samuel, and M. Singh, *J. Am. Chem. Soc.*, 1983, **105**, 6354.

[85] H. H. Hub, B. Hupfer, K. Horst, and H. Ringsdorf, *Agnew. Chem., Int. Ed. Engl.*, 1980, **19**, 938.

[86] A. Akimoto, K. Dorn, L. Gros, H. Ringsdorf, and H. Schupp, *Agnew. Chem., Int. Ed. Engl.*, 1981, **20**, 90.

[87] H. Bader and H. Ringsdorf, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 1623.

[88] K. Dorn, R. T. Klingbiel, D. P. Specht, P. N. Tyminski, H. Ringsdorf, and D. F. O'Brien, *J. Am. Chem. Soc.*, 1984, **106**, 1627.

[89] E. Lopez, D. F. O'Brien, and T. H. Whitesides, *J. Am. Chem. Soc.*, 1982, **104**, 305.

[90] C. M. Paleos, C. Christias, G. P. Evangelatos, and Ph. Daïs, *J. Polym. Sci., Polym. Chem. Ed.*, 1982, **20**, 2565.

[91] P. Tundo, D. J. Kippenberger, M. J. Politi, P. Klahn, and J. H. Fendler, *J. Am. Chem. Soc.*, 1982, **104**, 5352.

[92] P. Tundo, D. J. Kippenberger, P. L. Klahn, N. E. Prieto, T. C. Jao, and J. H. Fendler, *J. Am. Chem. Soc.*, 1982, **104**, 456.

[93] K. Kurihara and J. Fendler, *J. Chem. Soc., Chem. Commun.*, 1983, 1188.

[94] W. Reed, L. Guterman, P. Tundo, and J. H. Fendler, *J. Am. Chem. Soc.*, 1984, **106**, 1897.

[95] J. H. Fendler and P. Tundo, *Acc. Chem. Res.*, 1984, **17**, 3.

[96] J. Fendler, *Science*, 1984, **223**, 888.

[97] T. Kunitake, N. Nakashima, T. Takarabe, M. Nagai, A. Tsuge, and H. Yanagi, *J. Am. Chem. Soc.*, 1981, **103**, 5945.

[98] M. F. Roks, H. G. J. Visser, J. W. Zwikker, A. J. Verkley, and R. J. M. Nolte, *J. Am. Chem. Soc.*, 1983, **105**, 4507.

[99] J. H. Fuhrhop, D. Fritsch, B. Tesche, and H. Schmiady, *J. Am. Chem. Soc.*, 1984, **106**, 1998.

[100] L. Gros, H. Ringsdorf, and H. Schupp, *Agnew. Chem., Int. Ed. Engl.*, 1981, **20**, 305.

[101] D. Babilis, Ph. Daïs, L. H. Margaritis, and C. M. Paleos, *J. Polym. Sci., Polym. Chem. Ed.*, in press.

has been established that not only do they retain the structure of their monomeric counterparts but that they also exhibit enhanced stability, being less permeable than the respective monomeric ones. Stable vesicles are extremely useful, primarily in the construction of photochemical energy converters and to a lesser extent in their application as drug carriers.

The structures and properties of polymerized vesicles are affected by the position, the number, and the nature of the polymerizable group(s) (such as vinyl, acrylate, methylacrylate, diacetylene). Thus, in some polymerized vesicles the head-group mobility is preserved whereas in others the chain mobility is preserved, as shown diagramatically[100] in Figure 11. The introduction of two vinyl groups may lead to extra stabilization through crosslinking of the adjacent layers of the vesicles. This has been accomplished by the polymerization of monomeric vesicles of di(undecenyl) phosphate[90] to polymerized vesicles. Their stability (they had still not precipitated three years after their formation) is very probably attributed to the following crosslinked structure (Figure 12). A 50% polymerization of the monomeric vesicles was achieved.

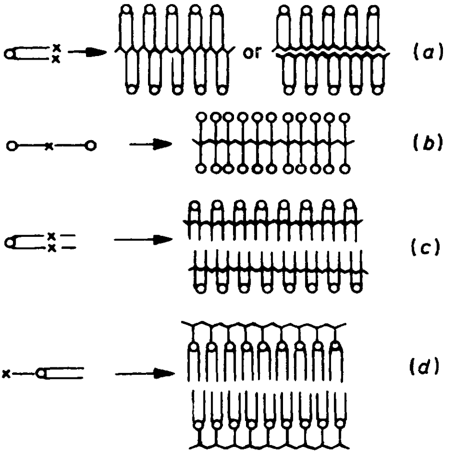

Figure 11 *Formation of polymerized vesicles with preservation of head groups mobility* (*a*—*c*) *or chain mobility* (*d*)
(Taken from L. Gros *et al.*[100])

The stabilization of polymerized vesicles is not always so straightforward. For example it has been found that of the allyl and diallyl vesicle-forming quaternary ammonium salts [(4) and (5)][101] only the diallyl polymerized vesicles prepared by a mechanism involving alternate intramolecular and intermolecular growth steps[102,103] exhibit such excellent stability. Polymerized vesicles originating from

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[102] G. B. Butler and R. J. Angelo, *J. Am. Chem. Soc.*, 1957, **79**, 3128.

[103] G. B. Butler in 'Polymeric Amines and Ammonium Salts', ed. E. J. Goethals, Pergamon Press, Oxford—New York, 1980, p. 125.

[104] P. Tundo, K. Kurihara, D. J. Kipperberger, M. Politi, and J. H. Fendler, *Agnew. Chem., Int. Ed. Engl.*, 1982, **21**, 81.

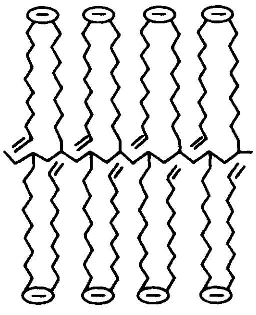

Figure 12

allyl derivatives are unstable and they dissipate shortly after irradiation. It seems that the insertion of piperidine[102,103] or rather pyrrolidone moieties[104a] into the backbone of diallyl polymerized vesicles has a profound effect on the stability of the vesicles. On the other hand, monomers bearing the diacetylenic polymerizable group[81,105] in the middle of their molecules polymerize in the vesicular phase according to Scheme 5 and afford extremely rigid structures which do not, however, show thermotropic phase-transitions.[105] This indicates that these particular polymerized vesicles have lost the smectic character of biological membranes.

A novel approach to the formation of polymerized vesicles is by the oxidation of a thiol group introduced into an appropriate vesicle-forming molecule. Such a 'monomer' is 1,2-bis(11-mercaptoundecanoyl)-*sn*-glycero-3-phosphocholine (6),[84] the bilayer of which is 'switched on' (polymerized) by oxidation and 'switched off' (depolymerized) by reduction, *i.e.* the reversibility of the system is governed by the thiol–disulphide redox cycle. Using this system biochemical studies could be carried out either in the 'on' polymerized or 'off' non-polymerized mode.

A completely different approach to the formation of polymerized vesicles is through the use of ionene polymers[97] prepared by the interaction of long-chain dibromides with ditertiary amines according to the reaction shown in Scheme 6. A segment of the vesicle structure consisting of ionic and lipophilic functions is also shown. This method of vesicle formation is probably the answer to the question: is the formation of polymerized vesicles exclusively associated with the polymerization from the vesicular phase, or may the polymer be prepared under conventional isotropic conditions and then subjected to one of the usual methods of

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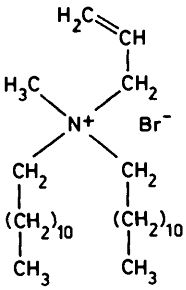
[104a] R. M. Ottenbrite in 'Cyclopolymerization and Polymers with Chain Ring Structures', ed. G. B. Butler and J. E. Kreta, ACS Symposium Series, No. 195, American Chemical Society, Washington D.C., 1982. Also, author's own unpublished data.

[105] H. Koch and H. Ringsdorf, *Makromol. Chem.*, 1981, **182**, 255.

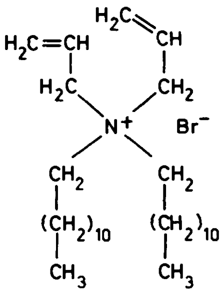
[106] D. Day, H. H. Hub, and H. Ringsdorf, *Isr. J. Chem.*, 1979, **18**, 325.

[107] B. Hupfer, H. Ringsdorf, and H. Schupp, *Makromol. Chem.*, 1981, **182**, 247.

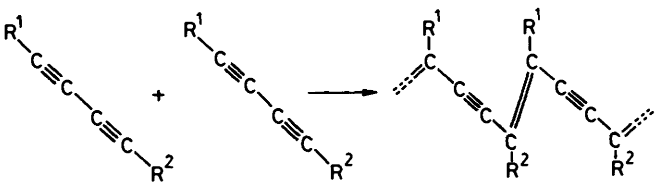
[108] K. Dorn, E. V. Patton, R. T. Klingbiel, D. F. O'Brien, and H. Ringsdorf, *Makromol. Chem., Rapid Commun.*, 1983, **4**, 513.



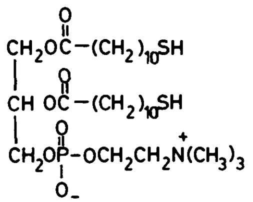
(4)



(5)



Scheme 5



(6)

vesicle formation?[109] Judging from this case (ionene polymers) one may assume that polymerized vesicle-formation is not limited to the topochemical mode of synthesis. Actually, there is no way in which dibromides and ditertiary amines could be aggregated into vesicular structures. At the present time, however, there is no experimental evidence, as far as vesicle formation is concerned, from a polymer prepared by addition polymerization in isotropic media.

Until recently the emphasis in most of the publications concerning polymerization in vesicular media was on the synthesis of diverse vesicle-forming monomers, the conditions of their polymerization to the respective polymerized vesicles, and

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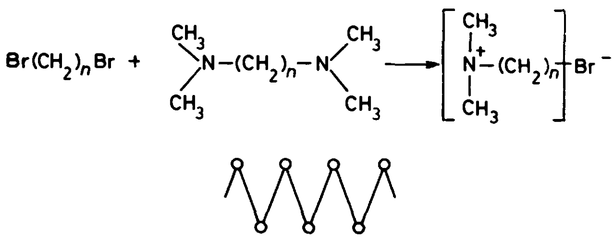
[109] S. Szoka and D. Papahadjopoulos in 'Liposomes: Physical Structure to Therapeutic Applications', ed. C. G. Knight, Elsevier/North-Holland Biomedical Press, Amsterdam.



Scheme 6

on their characterization (primarily stability[7,110] and permeability[7,110]). However, a systematic work on the kinetics and mechanism of photopolymerization in vesicular media was reported quite recently.[94] The study involved a styrene-containing monomer (7) which allowed the polymerization to be conveniently monitored by absorption spectrometry.

$$[n\text{-}C_{15}H_{31}CO_2(CH_2)_2]_2\,N^+[CH_3][CH_2C_6H_4CH{=}CH_2]\,Cl^-$$

(7)

Thus, continuous irradiation of the monomer or irradiation by laser pulses leads to a decrease in styrene absorbance by a first order process. The calculated rate-constants were independent of the vesicle concentration (vesicles unlike micelles do not break down on dilution) but increased linearly with increasing intensity of laser pulses. Rates of monomer disappearances were considerably slower in ethanol than in vesicles and, in contrast to the vesicular polymerization, depended on monomer concentration. This last observation and the fact that the sizes of vesicles remained practically unchanged on polymerization suggest the occurrence of intravesicular surface polymerization at an apparent reduced dimensionality and analysed on per vesicle rather than on volume basis. As a first approximation a polymerization model is considered, in which the vesicle surface is assumed to be hexagonally packed, each monomer being surrounded by six monomers. The photoinitiated free-radical can react with any one at its neighbours to initiate polymerization, to disproportionate, or to form non-polymeric products or alternatively the free radical may return to the ground state or react with oxygen impurity or the wall of the reacting vessel. Related to this photopolymerization, the same intravesicular model provides an experimentally measurable quantity which relates average polymer chain length (*i.e.* 20 ± 30% monomer per chain) to the quantum efficiency of the free-radical formation. In contrast to this short average polymer chain-length it was found[108] that two methacryloyl monomers, α-MA (8) and ω-MA (9), which were polymerized catalytically, exhibited chain lengths consisting of about 500 units. For poly(α-MA) the calculated number of

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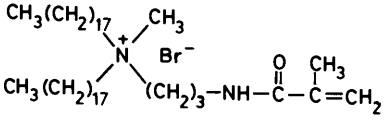
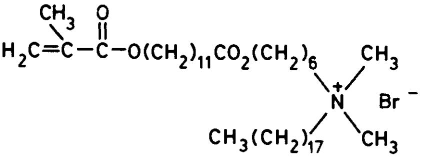
[110] R. Büschl, T. Folda, and H. Ringsdorf, *Makromol. Chem.*, 1984, Suppl. **6**, 245.

monomers per vesicle was 10^4—3×10^5 and therefore there must be about 20—600 chains per vesicle, while poly(ω-MA) with a number of monomers per vesicle equal to 10^4—8×10^4 contained 20—60 chains per polymerized vesicle. Also, preliminary experiments showed that $\bar{M}$ of poly(α-MA) varies inversely with the sonication time before polymerization. These results suggest that lower molecular weight polymers are formed with smaller vesicles. We may therefore envisage polymerized vesicles as consisting of several polymeric fragments and not, for example, of only two polymeric chains resulting from the polymerization of each layer, as is the case with one-compartment vesicles. This structure of polymerized vesicles is in some way encountered in intermolecular micelles[70] consisting of polymeric chains (each being an intramolecular micelle) aggregated to above bigger aggregates.



α - MA

(8)



ω - MA

(9)

6 Summary and Outlook

From the above discussion it is clear that the monomer organization in general affects polymerization and polymer properties. At the present time, however, it is not always possible to predict the nature and extent of the effects. It seems that this difficulty originates from a limited knowledge of the degree of organization in the various organized systems. Further systematic work on appropriately designed monomers, the organization of which is more definitely known, is required in order to predict and/or to maximize the organizational effects on polymerization.

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