Viscosity- and Inertia-Limited Rupture of Dextran-Supported Black Lipid Membranes

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We study the rupture of polymer-supported black lipid membranes (BLMs). The irreversible rupture of membranes is triggered by application of short transmembrane voltage pulses. The rapid membrane discharge during rupture permits the evaluation of the kinetics of defect widening. The linear increase of the membrane conductance in time during the rupture process indicates that the widening is determined by the inertia of the BLMs. Defects in polymer-free BLMs increase in size with about 20 cm/s. To decrease the rupture velocity of the membranes we attach high-molecular-weight dextran derivatives via hydrophobic dodecyl anchor groups to the BLMs. The density of the hydrophobic anchor groups along the polymer chains is found to be of considerable influence: While dextran with a low anchor-group density slows down the inertia-driven rupture process of BLMs, dextran with higher anchor-group density alters the kinetics and causes an exponential increase of the membrane conductance, suggesting a viscosity-determined rupture process. Dextran derivatives of medium anchor-group density show a transition from a viscosity- to an inertia-limited rupture.

Introduction

Early investigations on the rupture of ultrathin films were done on planar soap films.[1−5] Soap films of macroscopic size can be formed in air and permit the recording of the defect-widening optically.[4,5] Much thinner films containing only a bimolecular layer of well-defined structure are prepared by spanning a lipid membrane across a circular hole in an aqueous phase. The rupture of these membranes is triggered by applying an electric field across the membrane. Most of these electroporation studies focus on the action of electric fields on the lifetime of the bilayer and yield, for example, information about its energy barrier against rupture.[6−11]

For a better understanding of the rupture process, we adapted an electroporation method which allows us to follow the defect widening by recording the membrane conductance with a time resolution below 1 μs.[12−17] In more detail, we apply single voltage pulses across the membrane and record the discharge process of the pore. By increasing the voltage in small steps we induce single defects. The time course of the discharge process allows an indirect conclusion on the kinetics of the defect widening. On the basis of this technique we previously investigated membranes made of neutral or charged lipids under various conditions.[13−14,16] All these membranes showed a linear increase in membrane conductance with time during rupture.[12−14,16] From the observed linear increase, a constant radial pore-widening velocity is obtained, suggesting an inertia-driven rupture kinetics. A similar behavior was observed during the bursting of soap films 30 years ago.[3] A defect in such films widens with constant speed, whereas the film outside the rim remains undisturbed. These membranes are supposed to be under an homogeneous stress σ (twice the interfacial stress) which falls as a step function to zero at the edge of the pore. The corresponding force f_α^σ acts on the edge of the defect and drives the opening[3,14]

$$f_a^\sigma = 2\pi a\sigma \tag{1}$$

where a is the pore radius. f_a^σ is counterbalanced by the change in the momentum of the excess membrane material of the relaxed part, which is found in a tiny rim around the pore. Under the assumption of a constant opening velocity da/dt, the change in the momentum yields the force at the edge acting against the motion of the material

$$f_a^{\text{kinetic}} = -2\pi a\left(\frac{\mathrm{d}a}{\mathrm{d}t}\right)^2 \rho h \tag{2}$$

with ρ as density and h the film thickness. Balancing the forces of eqs 1 and 2 gives the rupture velocity da/dt of a film in the inertia-dominated regime:[3,14]

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \sqrt{\frac{\sigma}{h\rho}} \tag{3}$$

The experimentally found rupture velocity of soap films of about 10 m/s is in good agreement with the theoretical prediction of eq 3.[18] In contrast, our electroporation experiments on BLMs yield considerably smaller radial pore-widening velocities. Depending on the lipid composition the obtained velocities are in the range of 0.05−0.3 m/s.[16] To describe this behavior a dimensionless parameter ϕ has to be introduced to account for the unknown material flow and for dissipative effects:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \sqrt{\frac{\sigma\phi}{h\rho}} \tag{4}$$

Currently, we are studying systematically the influence of surface-attached high-molecular weight polymers on the stability and rupture kinetics of BLMs.[15,17] We showed previously that F-actin polymerized on stearylamine-containing DPhPC BLMs

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(1:9) reduces the radial pore-widening velocity of the membranes by several orders of magnitude. Most interestingly, the discharge curves of these membranes suggest an exponential increase of the pore radius in time instead of a linear one.[12−14,17] Recently, a similar behavior was observed optically in free-standing highly viscous poly(dimethylsiloxane) films of several micrometers thickness.[19] Possibly, the radial material flow in such films is not limited by inertia, but by their surface viscosity η. The force at the edge of pore in a BLM of an high surface viscosity

$$f_a^{\eta} = -8\pi\eta \frac{da}{dt} \tag{5}$$

has to be balanced by f_a^{σ} of eq 1. Obviously, this yields an exponential increase of the pore size in time

$$a(t) = a_0 \exp(\sigma/4\eta)t \tag{6}$$

In a viscous film, the rupture velocity should increase first exponentially up to a limiting radius R_c. Above this so-called crossover-radius, the further rupture should be determined by inertia. Beyond the critical radius R_c the pore should increase with constant velocity. R_c can be calculated with the constant rupture velocity $(da/dt)_{in}$ observed in the inertial driven process

$$R_c = \left(\frac{da}{dt}\right)_{in} \frac{4\eta}{\sigma} \tag{7}$$

We observed such a transition most recently with polylysine-decorated diphytanoyl-phosphatidylserine (DPhPS) BLMs.[17] However, in the previous study the transition occurred at small pore radii and it was impossible to shift R_c to higher values. Therefore we decided to trigger the transition by using polymers which promise to cause an higher surface viscosity and inertia in BLMs. We replaced in the present study polylysine with an high-molecular-weight dextran to which different amounts of *n*-dodecyl chains were covalently linked. While the hydrocarbon anchors of these polymers are able to insert into the hydrophobic core of a lipid membrane, the hydrophilic polymer backbone prefers to stay in the water phase. We demonstrate that the polysaccharide modifies the mechanical properties of BLMs in a dodecyl−dextran ratio dependent manner. The attached dextran reduces the rupture velocity of the membranes enough to shift the rupture process from the inertia to the viscosity-dominated regime.

Materials and Methods

Lipids and Electrolytes. Diphytanoyl-phosphatidylcholine (DPhPC) was purchased from Avanti Polar Lipids (Alabaster, AL) with purity >99% and used without further purification. The electrolyte contained ion-exchanged water (NANOpure, Barnstead) with specific resistance >17 MΩ-cm and 100 mM KCl (p.a.) from Merck (Darmstadt, Germany). The membrane-forming solution contained 1 wt % DPhPC in *n*-decane (p.a.) from Fluka (Buchs, Switzerland). The solution used for prepainting contained 1 wt % DPhPC in chloroform (p.a.) from Merck.

Synthesis of *n*-Dodecyl−Dextran. Dimethyl sulfoxide (DMSO) (p.a.) and pyridine (purum) were purchased from Fluka, distilled over CaH_2 and stored over a molecular sieve. About 4 g of dextran (from *Leuconostoc mesenteroides*, M_r = 200.000, Fluka) was dissolved in 100 mL of the DMSO and 8 mL of the dry pyridine at 60 °C. Dodecyl isocyanate (99%, Aldrich) was added without further purification after the polysaccharide dissolved completely. To obtain a degree of modification of 6%, 3% and 1% 0.32, 0.16, or 0.05 g dodecyl isocyanate was added to the solution. The reaction mixture was stirred under argon at 60 °C for 24 h and then given in 1.5 L acetone (>99%, Fluka). The solution/precipitation process was repeated two times. The white material was dried in a vacuum at 60 °C for several days.

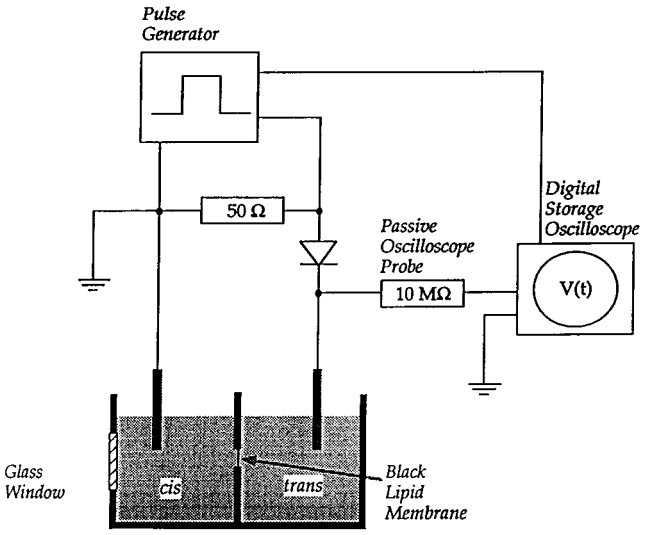

Figure 1. Scheme of the charge−pulse instrumentation to induce and record irreversible breakdown of planar lipid membranes.

Prior to measurements, 10 mg of the polymers was dissolved overnight in 1 mL DMSO. In the following we use the abbreviation dodecyl-dextran-6, dodecyl-dextran-3 and dodecyl-dextran-1 for the three modified polysaccharides corresponding to their degree of modification.

Formation of Black Lipid Membranes. BLMs of ∼1 mm diameter were formed according to Mueller et al.[21] Briefly, a Teflon cuvette containing two chambers was prepainted around the hole connecting both chambers with about 1 μL of the prepainting solution. The cuvette was allowed 20 min for drying and was filled afterward with the electrolyte containing 0.06 g/L of the respective polymer. An amount of 1 μL of the membrane-forming solution was spread on a Teflon loop and painted across the hole leading to a separation of both chambers by a lipid membrane. The thinning of the membrane could be observed through a glass window in the front side of the cuvette by a microscope (60-fold magnification). Optical inspection of BLMs formed in the presence of dodecyl-dextran-3 and -6 showed immediately after painting interference colors. It took about 20−40 min until the membranes showed an homogeneous black, suggesting that the thinning process of the films is slowed by the polymers. The quality of the BLMs is finally tested via a measurement of the electrical capacitance.

Electroporation Setup. Membrane rupture was initiated with the charge−pulse method previously described.[12,14] The experimental setup is shown in Figure 1. The Ag/AgCl electrode in the trans compartment is connected to a fast-pulse generator (Tektronix PG 507) through a diode (reverse resistance ≫ 10^{11} Ω). The voltage between the cis and trans electrode is recorded on a digital storage oscilloscope (LeCroy 9354A).

Prior to rupture, the membrane capacitance is determined by charging the BLM to a voltage of about 100 mV with a rectangular pulse of 10 μs duration. The value of the membrane capacitance is calculated from the *RC*-time constant of the exponential discharge process of the membrane across the 10 MΩ resistance of the passive oscilloscope probe. An irreversible

breakdown is initiated by charging the membrane with rectangular 250−600 mV voltage pulses of 10 μs duration. To avoid formation of multiple pores, we start to charge the membrane with a small voltage pulse of 250 mV. Then we raise the applied voltage in 20 mV steps applying five pulses per step until the membrane disrupts. In a typical rupture experiment about 20−100 pulses are applied prior to membrane rupture.

As long as the defect is small relative to the total area of the membrane, the bilayer capacitance can be considered as constant. Under this assumption the membrane conductance, $G(t)$, can be calculated via[12,14]

$$G(t) = \frac{I(t)}{U(t)} = \frac{1}{U(t)} \cdot \frac{\mathrm{d}Q(t)}{\mathrm{d}t} = \frac{1}{U(t)} \cdot \frac{-\mathrm{d}(CU(t))}{\mathrm{d}t} = \frac{-C}{U(t)} \frac{\mathrm{d}U(t)}{\mathrm{d}t} = -C \frac{\mathrm{d} \ln U(t)}{\mathrm{d}t} \quad (8)$$

where $I(t)$ is the discharge current, $U(t)$ the transmembrane voltage, $Q(t)$ the charge excess on one side of the membrane, and C the membrane capacitance. The minus sign indicates discharging of the membrane.

In our study the recorded conductance is larger than 10^{-5} S and caused by one or relatively few pores. Such pores have a large radius in comparison to the membrane thickness. This simplifies the relation between the pore radius and the pore conductance. The conductance $G_{\mathrm{pore}}(t)$ of a pore can be approximated by the inverse access resistance

$$G_{\mathrm{pore}}(t) = \frac{1}{R_{\mathrm{pore}}} = 2\kappa a(t) \quad (9)$$

where κ is the specific conductance of the electrolyte.[20] In case of single pores $a(t)$ corresponds to the pore radius, whereas for multiple pores $a(t)$ corresponds to the sum of all radii.

A defect-free membrane can be considered as a perfect isolator. Under the chosen experimental conditions the measured conductance is due to the 10 MΩ resistor of the passive oscilloscope probe and possible defects in the membrane. If the latter become the dominant source of conductance, a combination of eqs 4, 8, and 9 then yields the following expression for the radial rupture velocity

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \frac{-C}{2\kappa\left(\frac{\mathrm{d}}{\mathrm{d}t} \ln U(t)\right)} \quad (10)$$

A typical time course of the transmembrane voltage during rupture is shown in Figure 2a. The membrane was made of DPhPC in a 0.1 M KCl and dodecyl-dextran-1-containing aqueous phase. An externally applied voltage pulse charged the membrane during 10 μs to a transmembrane voltage of about 530 mV. This stage is followed for about 10 μs by a steep, not well understood voltage drop. This nonideal region is followed by an exponential decay of the voltage due to discharging of the membrane via the parallel 10 MΩ resistor of the passive oscilloscope probe. In this region the *RC*-time constant yields information on the capacitance of the membrane. The defect formation is seen in curve 2a by a sharp kink after about 0.6 ms. This kink is followed by a superexponential voltage decay indicating the rupture of the membrane.

From this curve three different quantities can be determined. The first one is the so-called delay time which is the time interval between the end of the externally applied voltage pulse and the onset of the superexponential decay of the voltage curve. In case of Figure 2a the delay time equals about 0.6 ms. The second quantity is the breakdown voltage causing irreversible rupture of the membrane. We define as breakdown voltage the magnitude of the voltage when the voltage decay starts to follow the *RC* behavior. In Figure 2a, for example, a breakdown voltage of about 525 mV is read. As third characteristic quantity we obtain the conductance increase due to defect formation by analyzing the voltage versus time curves according to eq 8.

Results

At the beginning of this study, we tested different membrane-forming procedures. The most reproducible results were obtained by injecting the dissolved polymers into the electrolyte prior to the formation of the lipid film. We used throughout all experiments a 0.06 g/L dextran-containing bulk phase. Dodecyl-dextran-3 and -6 were found to slow the thinning process of the film significantly. About 20−40 min after painting of the film, all surface-decorated membranes had a electric capacitance similar to BLMs formed in a polymer-free electrolyte. No stable BLMs of reasonable high capacitance were obtained with the double or higher concentrations of dodecyl-dextran-3 or -6. However, at polymer concentrations lower than 0.06 g/L the rupture behavior of the BLMs is unambiguously related to the polymer concentration of the aqueous phase: While high dextran concentrations affect strongly the rupture process, low concentrations cause only small alterations to polymer-free BLMs (data not shown).

A different procedure is to add the modified dodecyl−dextran to preformed DPhPC membranes. Under this condition the optical appearance and electric capacitance of these BLMs did not change over several hours. However, the BLMs requiered 1−5 h to show the rupture behavior typically observed in membranes formed according to the procedure described above. This suggests that polymer adsorption and insertion is the time-limiting step for the formation of a homogeneous decorated membrane.

To study the effect of the different dodecyl−dextrans on the mechanical stability, we determined the breakdown voltages. For a pure DPhPC membrane an average breakdown voltage of 530 mV was obtained (Table 1). Injection of unmodified dextran into the electrolyte did not affect at all the breakdown voltages. In contrast the breakdown voltages of the polymer-decorated BLMs depend on the dodecyl−dextran ratio of the polymers. DPhPC membranes formed with dodecyl-dextran-1 decrease the average breakdown voltage to ∼420 mV, dodecyl-dextran-3 to ∼390 mV, and dodecyl-dextran-6 to ∼310 mV.

Also, the rupture kinetics is drastically affected by polymers of high dodecyl−dextran ratio. Pure DPhPC BLMs show a linear increase of the conductance with time after the defect occurred. This increase remains unchanged in the presence of dextran or dodecyl-dextran-1. Equation 9 allows the evaluation of the radial pore-widening velocity from the conductance increase. Inserting a bulk conductance of 1.4 S/m for a 100 mM KCl containing electrolyte our model yields for polymer-free-, dextran-, and dodecyl-dextran-1-containing BLMs rupture velocities of 20 ± 2 cm/s (Figure 2).

In contrast, the presence of dodecyl-dextran-6 causes an exponential increase in conductance after rupture occurred. Due to the drastically decreased rupture velocity of the membranes their rupture process can be recorded by our method 10−50-fold longer compared to that of undecorated membranes. Table 2 summarizes the experiments of the DPhPC/dodecyl-dextran-6 series. Assuming a typical surface tension in a BLM of about 2 mN/m[14] allows the determination of the surface viscosity the membranes to (0.5−8) × 10^{-7} Ns/m. It is interesting to note

TABLE 1: Average Membrane Capacitance, Breakdown Voltages, Rupture Velocities, and Membrane Viscosities of the Various BLMs Investigated in This Study[a]

	delay time (μs)	breakdown voltage (mV)	membrane capacitance (nF)	surface viscosity (10^{-7} Ns/m)	number of experiments
DPhPC	85 ± 20	530 ± 10	0.61 ± 0.02		40
DPhPC + dextran	120 ± 45	510 ± 12	0.6 ± 0.02		10
DPhPC + dodecyl-dextran-1	490 ± 240	416 ± 24	0.78 ± 0.02		10
DPhPC + dodecyl-dextran-3	1039 ± 200	388 ± 13	0.73 ± 0.02	$\leq 0.5 \times 10^{-7}$	11
DPhPC + dodecyl-dextran-6	1940 ± 370	310 ± 11	0.63 ± 0.04	$(3 \pm 0.7) \times 10^{-7}$	12

[a] The aqueous medium contained 100 mM KCl; $T = 295$ K. Errors given are standard errors.

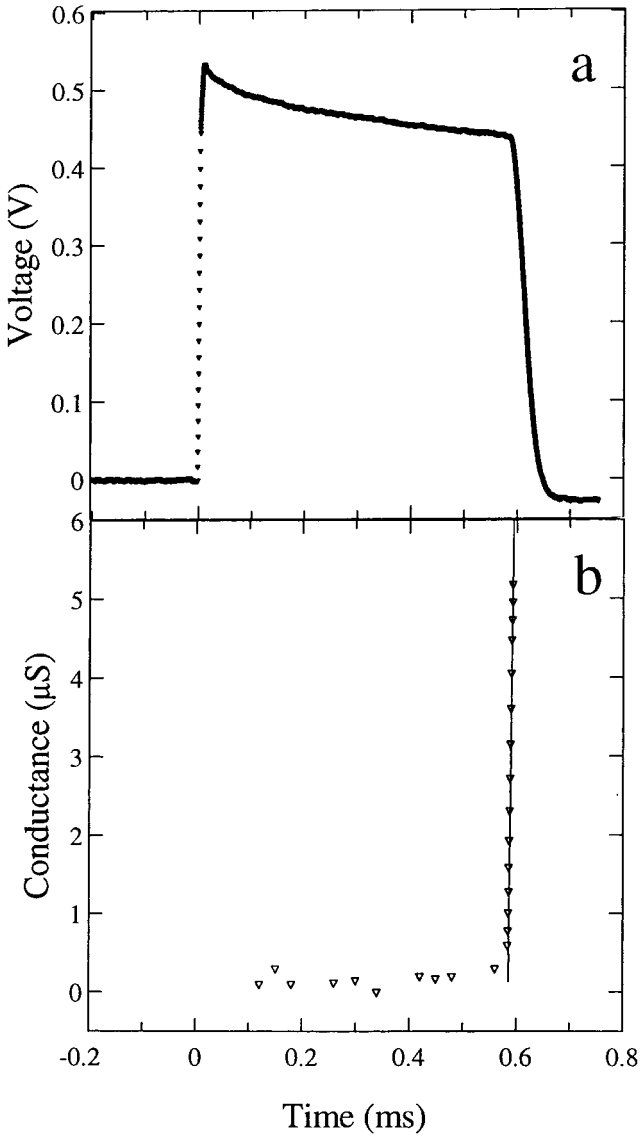

Figure 2. (a) Time course of the transmembrane voltage during electric-field-induced irreversible rupture of a DPhPC membrane. The length of the applied voltage pulse was 10 μs. The aqueous phase contained 100 mM KCl and 10 g/L dodecyl-dextran-1; $T = 295$ K. (b) Time course of the membrane conductance calculated from the voltage curve above. The solid line is a linear fit corresponding to a pore widening of about 20 cm/s.

that in our experiments the breakdown voltage, the surface viscosity, and membrane capacitance are not unambiguously correlated.

The conductance curves of membranes containing the dextran of medium anchor density, dodecyl-dextran-3, show considerably different time courses. Some of them neither follow a purely linear nor an exponential course (compare Figure 3). A close inspection of these curves suggests a two-kinetic process. The first part of these curves can be described by an exponential function, whereas the second part follows a linear course (Figure 4). The exponential regime allows us to evaluate surface viscosities of about $(1-5) \times 10^{-8}$ Ns/m. From the following linear part of these curves a radial pore-widening velocity of (2−10) cm/s is obtained. We attribute the reduced rupture velocities in the inertia-dominated regime to the increased momentum of the moving membranes. However, repeated measurements revealed also some conductance curves evolving purely linear or purely exponential within the time window of our method, indicating that films of considerably different viscosity and inertia were formed under similar experimental conditions.

TABLE 2: Overview about the Single Experiments of the DPhPC/Dodecyl-dextran-6 Series[a]

	delay time (μs)	breakdown voltage (mV)	membrane capacitance (nF)	surface viscosity (10^{-7} Ns/m)
1	320	390	0.61	1.16
2	1688	285	0.83	1.44
3	1462	370	0.61	2.07
4	2300	300	0.76	3.62
5	2962	290	0.81	1.14
6	1780	300	0.53	6.93
7	880	360	0.40	1.40
8	976	300	0.60	0.54
9	1269	280	0.54	1.56
10	5526	280	0.53	
11	1544	300	0.51	3.05
12	2562	312	0.83	8.21

[a] The quantities determined from a single rupture experiment are written in one row. The aqueous medium contained in all experiments 100 mM KCl, $T = 295$ K.

The third quantity which can be determined by our experimental setup is the delay time between the applied voltage pulse and the detection of a conductance increase. This quantity again seems to dependent on the dodecyl−dextran ratio of the adsorbed polymers. While pure DPhPC membranes and those in the presence of unmodified dextran typically show an average delay time of about 100 μs, BLMs in the presence of dodecyl−dextran show significantly larger values. They ranged from about 500 μs in the presence of dodecyl-dextran-1 and to about 2000 μs in the presence of dodecyl-dextran-6.

Discussion

The main advantage of free-standing BLMs is their well-defined and defect-free bilayer structure. Incorporated amphiphilic polymers such as the ones we have chosen for this study can alter this property significantly. The formation of a BLM in the presence of dextran derivatives slows down the

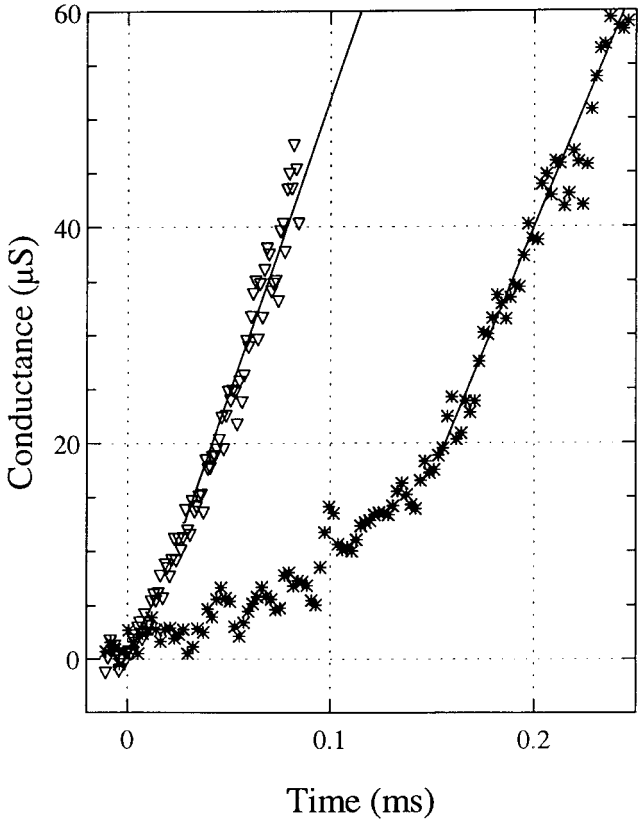

Figure 3. Time course of the membrane conductance during electric-field-induced irreversible rupture of a DPhPC membrane in the presence of dodecyl-dextran-1 (∇ and in the presence of dodecyl-dextran-3 (*). The aqueous phase contained 100 mM KCl; $T = 295$ K. The symbols indicate the experimental data. The solid lines are linear fits.

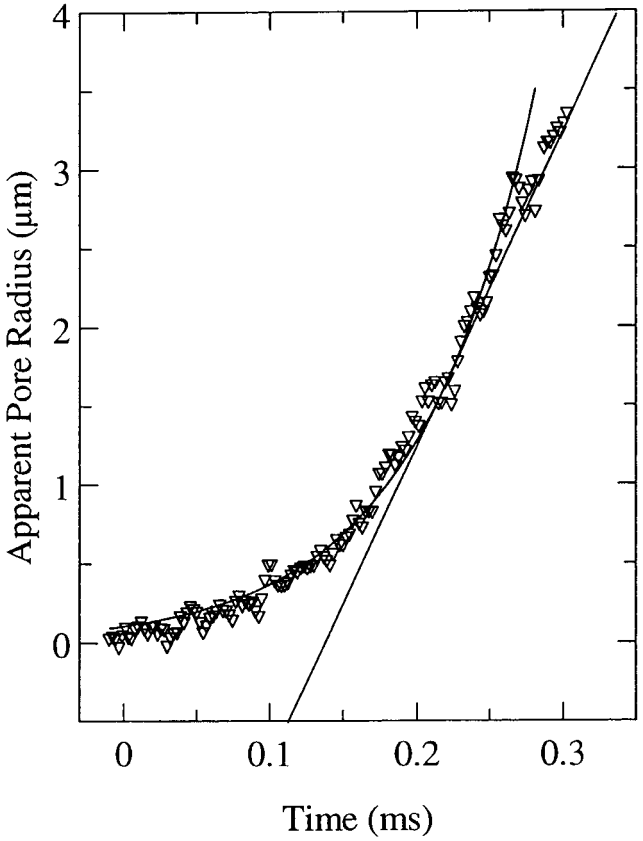

Figure 4. Time course of the apparent pore radius calculated according eq 9 from the DPhPC/dodecyl-dextran-3 curve shown in Figure 3. The symbols indicate the experimental data. The solid lines are an exponential and a linear fit.

process of thinning to the final bimolecular structure. To control the thinning process we recorded the electric capacitance of the membranes and observed them optically. We chose to add in the electrolyte a fixed polymer amount of 0.06 g/L. Our finding that the polymer-free and polymer-containing BLMs have the same capacitance for a given area suggests a similar thickness of their hydrophobic core. This implies that the polymer layer is fully permeable to the potassium ions of the electrolyte. Moreover, it can be concluded that the hydrocarbon core of the supported films is unchanged, since multilayered lipid structures should cause considerably smaller capacities. Therefore we assumed that our supported BLMs are polymer-decorated bilayered lipid membranes.

Our data show that dodecyl−dextran strongly alters the nature of the rupture process. As unmodified dextran does not affect the rupture process, we attributed our observations to the properties of the surface-attached polymer and not to modified bulk properties. The decrease of the breakdown voltages indicates that the attached polymer layer alters significantly the mechanical properties of the BLMs. On one hand the attached polymer might decrease the energy barrier necessary to form a pore, either by increasing the surface tension of the membrane or by reducing the edge energy of the pore. On the other hand the surface-attached polymer might stiffen the membrane. Dextran itself is known to be a branched and rather rigid polymer.[22,23] A closely attached dextran layer should therefore hinder undulation of BLMs. If an electrocompressive force is applied on such a BLM, the dissipation of this energy into undulation may be more difficult than in polymer-free BLMs. Interestingly, the influence of surface-attached polymers on the breakdown voltage of BLMs is in general more polymer-specific. Whereas the surface-attached dodecyl−dextran or electrostatically bound high-molecular-weight polylysine reduces the breakdown voltage of BLMs significantly, attached F-actin or low-molecular-weight polylysine does not affect their breakdown voltage.[15,17]

The main interest of this study was to modify the rupture kinetics of the BLMs by surface-attached polymers. The time-resolved conductance measurements gives information on rupture kinetics of the membranes. After formation of a defect the conductance suddenly increases either linearly or in case of dodecyl-dextran-6 exponentially in time. Equation 9 allows a straightforward conversion of the measured conductance into that of a pore with a radius a. This approach is based on the formation of a single pore of circular shape. The assumption of a single pore is supported by the statistics derived from a large number of membrane ruptures. We observed a distribution of the conductance increase around a minimal value and multiples of it. The minimal slope should correspond to the defect widening of a single one. If the conductance increase would be due to the widening of a large number of pores, no distinct minimal value but rather a wide distribution should be observed. Equation 9 is valid for a defect of circular shape. For small deviation from the circular one the conductance scales with the total edge length of the pore and our rupture velocity corresponds to that of the increase in edge. To date it was not possible to record optically the real shape during rupture as shown in case of larger macroscopic soap films.[5]

Evaluation of the conductance curves of polymer-free and dodecyl-dextran-1 containing membranes yield for both membrane types rupture velocities of (20 ± 2) cm/s, suggesting a similar momentum of the moving films. This suggests that only

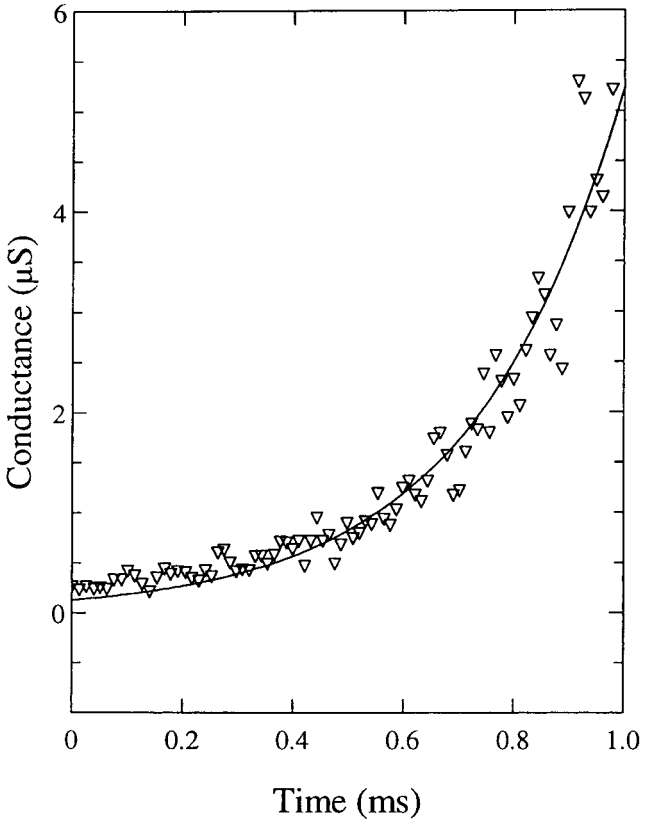

Figure 5. Time course of the apparent pore radius in the case of DPhPC/dodecyl-dextran-6. The symbols indicate the experimental data, and the solid lines correspond to an exponential fit.

small amounts dodecyl-dextran-1 are attached to the BLMs.[14] In contrast, dodecyl-dextran-6 changes the rupture kinetics of the membranes to that typically observed in highly viscous films (Figure 5). The pore widening of highly viscous films increases until the inertia of the membrane becomes the limiting factor. However, all membranes of the DPhPC/dodecyl-dextran-6 series are obviously too viscous to reach the linear regime within the time window of our method. In contrast some of the dodecyl-dextran-3 containing BLMs show such a transition. The fact that we observed only in some but not in all membranes such a behavior, suggests a broad distribution of the viscosity in the DPhPC/Dodecyl-dextran-3 series. Curves which show this transition allow the simultaneous evaluation of the surface viscosity and the pore-widening velocity of the inertial process. Figure 4 shows such an event. The curve allows us to evaluate the surface viscosity to 2×10^{-8} Ns/m, the velocity of the inertial process to 10 cm/s, and the crossover radius to 2 μm. It is interesting to note, that surface-attached F-actin and high-molecular-weight polylysine increase also the surface viscosity of BLMs.[15,17] We expect that a wide range of high-molecular-weight polymers, as well as dense layers of peripheral proteins, change the rupture kinetics of membranes in a similar way.

The interpretation of the delay-time is rather complex. With our experimental setup, we resolve only defects which have a similar or higher conductance than the 10 MΩ resistor placed in parallel to the membrane. Under the chosen experimental conditions, such a defect must have at least a diameter of ~20 nm. On the basis of a constant pore-widening velocity of 20 cm/s, a 20 nm defect should take less than 100 ns to be formed. Experimentally, at least 3 orders of magnitude higher average delay times are detected, suggesting a reduced ability of the lipid molecules to rearrange prior to the start of the pore to widen. Inspection of Table 1 confirms this consideration, as it reveals an unambiguous correlation of the average delay times and the dodecyl−dextran ratio of the adsorbed polymer. It is interesting to note, that a similar trend of the delay times was observed in the polylysine-decorated DPhPS BLMs. Here, the average delay times could be correlated to the degree of polymerization of the adsorbed polylysine. Interestingly, the surface viscosities and delay times in the dodecyl-dextran-6 series (Table 2) also show a correlation. Films of high surface viscosity tend to have long delay times and vice versa; even so, this trend is less pronounced than in case of polylysine. We conclude that the significantly prolonged lifetimes of the pores are due to mechanical properties of the immobilized polymers.

Conclusions

We have shown that high-molecular-weight dextran can be attached to black lipid membranes via dodecyl anchor groups. Electroporation of these membranes demonstrates that the surface-attached polymers drastically change the mechanical properties of the membranes. Increasing the dodecyl−dextran ratio of the polymer reduces the stability of BLMs significantly. Moreover, binding of dextran increases the inertia and viscosity of the membranes and so reduces their rupture velocity. For the first time it was possible to monitor the transition from a viscosity- to an inertia-dominated rupture processes.

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